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ON

THE QUANTUM THEORY OF X-RAY REFLECTION

AND

THE RAMAN REFLECTIONS OF X-RAYS IN CRYSTALS

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THE QUANTUM THEORY OF X-RAY REFLECTION: BASIC IDEAS

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1. Introduction

The phenomena arising when a beam of X-rays traverses a crystal and ascribable to the possible or actual movements of the atoms in it from their positions of equilibrium are of very great interest, since their study may be expected to throw light on the nature of such atomic movements and also on the nature of the interaction between the X-rays and the material particles of the medium. In the analogous case of a beam of monochromatic light traversing a transparent crystal, the phenomenon of the scattering of light with change of frequency first observed by the present writer in 1928 renders a direct spectroscopic investigation of the atomic vibrations possible. Much light has been recently thrown on the subject of crystal physics by such spectroscopic studies. Indeed, the new knowledge derived in this way necessitates a radical revision of the ideas hitherto accepted concerning the dynamics of crystal lattices and the thermal energy of crystals. Further, the optical investigations show very clearly that the interchanges of energy and momentum between the radiation and the crystal lattice are determined by the principles of the quantum mechanics and not by the

classical ideas. Early last year (1940), it was observed by Dr. P. Nilakantan and the present writer that the (111) crystal planes of diamond exhibit monochromatic X-ray reflections of a new type which are as sharply defined as the ordinary or Laue reflections but which obey a wholly different geometric law. Further, the intensity of these reflections, though definitely smaller than the intensity of the classical X-ray reflections, is of the same order of magnitude and is not appreciably altered by either rise or fall of the temperature of the crystal. These and other observations of a fundamental character revealed the existence of a whole group of X-ray phenomena which lie outside the scope of the existing theoretical developments of the subject. It thus becomes necessary to re-examine the assumptions on which the existing theories are based and to build a new theoretical structure in better accord with facts.

2. *The Failure of the Classical Mechanics*

In an essay on the molecular diffraction of light published in 1922, the present writer showed that, contrary to the opinion generally held at that time, transparent crystals such as quartz, rock-salt and ice traversed by a beam of light exhibit a true opalescence or diffusion of light associated with the ultimate structure of the crystal. This diffusion was provisionally attributed to the disordering of the crystal lattice by thermal agitation. The subsequent observation by the present writer that the spectrum of the light so scattered by crystals exhibits changes of frequency placed a new complexion on the matter. The incident light being monochromatic, frequency differences between the incident and scattered radiations are observed which fall in the infra-red region of the spectrum and are therefore to be identified with certain specific modes of vibration of the crystal structure. If the appearance of such vibrations in the spectrum of the scattered light had been due to thermal agitation in the crystal, it would follow from the principles of optics and electrodynamics that the radiations of *increased* and *diminished* frequencies should appear with *equal intensity*. Actually, this is very far from being the case. Indeed, when the frequency differences are large, we observe *only* scattered radiations with diminished and *none* of increased frequencies. These facts indicate that the vibrations of the crystal lattice revealed by the spectroscope are produced or induced by the light itself. Further, quantitative studies of intensity show that this is the correct view of the matter even if such vibrations are of sufficiently low frequency to be appreciably excited by thermal agitation. The light induces a step-down or a further step-up of the vibration as the case may be, appearing as scattered light with increased

and diminished frequencies respectively, though with greater intensity corresponding to the greater amplitude of vibration. The facts thus compel us to recognise that the observed scattering of light is in every case associated with the changes in the energy level of vibration induced by the light itself.

The spectroscopic evidence thus makes it clear that the scattering of light in crystals is a quantum-mechanical effect, the exchanges of energy between the photons and the crystal lattice occurring in discrete units or quanta of vibrational energy. When these units of energy are sufficiently small, in other words when the frequencies of mechanical vibration of the crystal lattice are sufficiently low, the quantum-mechanical picture of the facts tends asymptotically towards the purely classical picture in which the scattered light should appear with equal intensity with increased and diminished frequencies. In other words, the quantum description has a classical analogue; the latter, however, bears no resemblance to the facts except when the vibrations of the crystal are of very low frequency or the temperature of the crystal is very high. The lower the temperature of the crystal, and the higher the frequency of a particular vibration, the less would the actual facts resemble the picture suggested by the classical ideas.

That the propagation of X-rays through a crystal is influenced by the atomic vibrations is shown by the diminishing intensity of the spots in a Laue pattern when the crystal is heated. Numerous physicists, amongst them Debye (1914), Brillouin (1922), Waller (1923, 1927), and Laue (1926), have considered this problem from a semi-classical point of view. Laue in his memoir of 1926 drew attention to a very important feature emerging from his treatment of the problem, namely that all secondary radiations from the crystal, except those appearing as the geometric reflections by the lattice planes, suffer a change of frequency. The origin of this change of frequency is readily understood. An atom occupying a fixed position in space would naturally emit secondary radiations having the same frequency as the primary X-ray falling upon it. An oscillation of the atom about its position of equilibrium would result in a periodic variation of phase of such secondary radiation. The analysis indicates that the secondary radiations would then include components with their frequency increased and diminished respectively by the oscillation frequency of the atom. These components appear with an intensity which rapidly increases with the amplitude of the atomic vibration, the intensity of the component of unmodified frequency diminishing *pari passu*. Laue emphasised that these changes of frequency play a fundamental rôle in determining the observed optical effects. For, only such radiations as have identically the same

frequency can be coherent with each other; any difference of frequency however small would render coherence impossible. A frequency analysis of the secondary radiations and therefore also of the atomic vibrations is thus a necessary preliminary to a proper investigation of the problem.

Laue showed that the secondary radiations from the atoms in the crystal vibrating with a specified frequency yield a resultant in which the *components with increased and diminished frequency appear superposed with identical intensity*. The situation is thus exactly similar to that arising in the theory of the scattering of light in a crystal when considered classically, and it automatically follows that the classical mechanics must also fail in the X-ray problem. The change over from classical to quantum mechanics is fortunately simple. The conservation of energy as between the X-ray quantum and the crystal is equivalent classically to a change of frequency of the radiation, such change, however, occurring in one direction or the other and not in both at once. The conservation of momentum in the encounter between the X-ray quantum and the crystal is equivalent classically to the usual formula for a monochromatic reflection of incident radiation by a stratified medium, the stratifications being now dynamic and not static. The correct intensity for the radiation of modified frequency resulting from the encounter is found by associating one energy quantum of the appropriate frequency with each degree of freedom of vibration of the crystal lattice. The effect of thermal agitation in the crystal enters into the quantum mechanical scheme for the X-ray problem in exactly the same way as in the parallel problem of the scattering of light.

3. *The Vibration Spectrum of a Crystal*

Einstein who was the pioneer in the development of the quantum theory of specific heats suggested that the vibrations of the atoms in a solid have *monochromatic* frequencies and showed how these frequencies could be connected with the observed variation of specific heat with temperature. He also explained how in simple cases the order of magnitude of these frequencies could be inferred from the elastic properties of the solid. The alternative hypothesis put forward by Debye, namely that the frequencies of atomic vibration in a solid form a continuous spectrum which may be identified with its elastic vibrations, subsequently however found its way into general favour. The success of the Debye formula in representing the course of the specific heat curve in several cases promoted the belief that the hypothesis correctly represents the actual vibration spectrum of simple solids. That this belief is illusory becomes evident on a closer examination of the facts.

In the first place, it may be pointed out that while a knowledge of the vibration spectrum enables us uniquely to determine the specific heat curve, it can scarcely be suggested that a knowledge of the specific heat curve enables us uniquely to determine the vibration spectrum. Indeed, whenever it has been possible to make a direct spectroscopic study of the vibration spectrum of a solid, the claim of the Debye hypothesis to represent the same is shown to be false. Taking for instance the case of diamond, the studies of Bhagavantam (1930) on the scattering of light in this crystal, and the recent investigations of Nayar (1941) on its luminescence at low temperatures show the lattice spectrum of diamond to consist of numerous discrete or monochromatic frequencies, some of them being much smaller than the so-called limiting frequency calculated from the Debye formula. The spectrum of the scattering of light in sulphur and phosphorus similarly exhibits numerous discrete lines, including some with very low frequency shifts, indicating that most of the degrees of freedom of atomic vibration are represented by monochromatic vibrations as originally pictured by Einstein. The position is equally striking when we consider crystals of apparently simple chemical composition, *e.g.*, quartz. Mr. Saksena (1940) has shown by a detailed investigation that no less than 24 out of every 27 degrees of freedom are represented in the vibration spectrum of this crystal by monochromatic frequencies.

It is known that the Debye formula fails to represent the specific heat curves correctly in several cases. It may be pointed out that these failures are actually more significant than the successes of the formula in other cases. Elaborate hypothesis have been put forward to explain away these failures, overlooking the simple explanation indicated by the spectroscope, namely, that the vibration spectrum of every crystal, however simple in its chemical composition, includes several monochromatic frequencies. When these frequencies are known, the specific heat formula necessarily contains corresponding Einstein terms, and this involves a reduction (usually very drastic) in the number of degrees of freedom allotted to the Debye term, as also of its "limiting frequency". In the case of diamond, for example, it is shown in a forthcoming paper by Mr. V. B. Anand that the specific heat data are perfectly expresssed in this way by the spectroscopically observed frequencies, only one-eighth of the total number of degrees of freedom being included in a term of the Debye type. On the other hand, a Debye function alone even with an arbitrarily assumed "limiting frequency" shows large deviations from the observed specific heats. It may reasonably be inferred that in other cases, *e.g.*, metallic silicon or grey tin, where the Debye formula altogether fails to represent the specific heat data, the cause of failure is the same,

namely that the vibration spectrum includes several monochromatic frequencies.

Thus, both the spectroscopic and specific heat data show unmistakably that the Debye picture of the vibration spectrum of a solid bears no resemblance to the facts, except in the region where it is *prima facie* appropriate, namely in respect of the elastic solid vibrations of the lowest frequencies whose wave-length is large compared with the lattice spacings of the crystal. The maximum possible contribution which such vibrations can make to the specific heat of the solid can be found by treating the lattice cell in the crystal as a single unit and assigning it three degrees of freedom of translatory movement. All other degrees of freedom of movement are necessarily associated with monochromatic or Einstein frequencies of vibration of the crystal structure. Thus, in all crystals, including even those which are elementary or of the simplest chemical composition, the vibration spectrum is essentially of the type pictured by Einstein, and consists of discrete or monochromatic frequencies lying in the infra-red or high-frequency region. This is accompanied in the region of low frequencies by a continuous spectrum of elastic vibrations. The contribution of the latter to the thermal energy would be relatively of minor importance for the vast majority of crystals except at the lowest temperatures.

4. Character of the Einstein Vibrations

We may now proceed to consider the nature of the monochromatic vibrations. It is evident that they arise from a periodic variation with time of the basic grouping of the atoms in the unit cells of the lattice. Such a vibration obviously cannot be confined to an individual cell, for its energy would then be rapidly passed on to the neighbouring cells and would be immediately damped out. We must, in fact, picture the vibrations as taking place simultaneously and in identically the same way in all the cells of the lattice. The frequency of such vibrations as well as their modes would be determined by the internal architecture of the crystal, in other words by the geometric grouping of the atoms and the forces which they exert on each other. If the number of the lattice cells be sufficiently large, as would be the case even for a sub-microscopic crystal, these frequencies and modes would be wholly independent of the size or shape of the crystal. The vibrations must, in the limiting case, be pictured as having an identical frequency, amplitude, and phase in all the cells of the lattice, as only then could the motion be truly monochromatic. Any variation in the phase of the vibration at different points in the crystal would involve a departure from perfect monochromatism, but this would be negligible provided the

phase wave-length is sufficiently great to include a large number of lattice cells. Phase wave-lengths comparable with the dimensions of the lattice cells would be altogether excluded, and in general the smaller wave-lengths would be much less probable than the larger ones for which the frequency is independent of wave-length. The possible orientations of the phase waves would be determined by the geometry of the atomic grouping and especially by its symmetry characters.

Turning now to the continuous spectrum of elastic or low frequency vibrations, the situation here is totally different. The atomic structure of the solid does not enter into the picture. The possible frequencies of vibration are explicitly determined by the macroscopic dimensions of the crystal and their relation to the velocity of the wave propagation, the spectrum extending continually towards lower frequencies as the dimensions of the crystal are enlarged. The frequencies vary with the wave-lengths, being inversely proportional to them. The possible wave-lengths being determined by the dimensions of the crystal, it follows from simple geometry that the cases in which the wave-lengths are small are much more numerous than those in which they are large. Further, the orientation of the wave-fronts is entirely arbitrary and bears no relation whatsoever to the symmetry characters of the crystal or its atomic architecture.

5. *The Fallacy of the Born Postulate*

As shown in the preceding pages, facts and principles alike compel us to reject the hypothesis of Debye as a description of the vibration spectrum of a crystalline solid except in the restricted region of low frequencies. We have also seen that these low-frequency vibrations are altogether different in their character from the vibrations of higher frequency lying in the infra-red region of the spectrum. It follows that any treatment of the problems of crystal dynamics based on the concepts of Debye is necessarily fallacious. It may be remarked that the basic idea underlying Max Born's crystal dynamics is essentially the same as that of Debye, namely that all the possible vibrations of a crystal lattice are analogous to the elastic vibrations, having the same distribution of the phase-waves in respect of the wave-lengths and their relation to the size of the crystal, as well as an identically similar distribution of the phase waves in respect of orientation in space. No proof or justification of this postulate seems ever to have been put forward. The so-called postulate of the "cyclic lattice" is in fact nothing more than an *ad hoc* hypothesis adopted for mathematical convenience. It is evident that this postulate is in total conflict with the conclusions at which we have arrived regarding the characters of the mono-

chromatic vibrations of the crystal lattice. We shall therefore proceed to examine the Born postulate critically with reference to its claims to represent the actual state of affairs in a crystal.

One of the most remarkable facts brought into evidence by the study of the scattering of light in crystals is the extreme sharpness of the lines observed in the spectra of such scattering. Even in those few cases where the spectrum exhibits bands having an observable breadth, these sharpen to the finest lines when the crystal is cooled down to low temperatures. A perfect monochromatism of the vibrations of the lattice in the infra-red region is thus to be regarded as a characteristic property of the crystalline state, at least under ideal conditions. Not only is this true in respect of such vibrations as are also observable with the substance in the molten or dissolved condition, but it is equally so in respect of such vibrations as are specially characteristic of the crystalline state. It is obviously impossible to reconcile this situation with the idea that these vibrations are of the same nature as the elastic vibrations giving a continuous spectrum of frequencies.

To exhibit the fundamental error in Born's postulate, we may consider the behaviour of a model consisting of N Planck oscillators of identically the same kind regularly arranged in geometric order inside a box. The postulate of Born assumes that the dynamic behaviour of these oscillators could be represented by a three-dimensional Fourier series whose wavelengths are sub-multiples of the dimensions of the box and in which all the terms have equal weight. The assumption is, *prima facie*, unjustifiable because we are not here concerned with possible translatory movements of the oscillators which would involve collisions with the walls of the box, but only with the internal oscillations of the individual units in fixed positions. Accepting the postulate however for a moment, we may consider its implications in regard to the behaviour of the oscillators in our model. The essence of a Fourier representation is that the summation of the terms can reproduce the most arbitrary kind of disturbance. In the present case, since the series contains the full number of terms, namely N, all of which have equal weight, it would mean that their superposition would result in the phases of the individual oscillators being entirely arbitrary and uncorrelated with each other. This is evidently a *reductio ad absurdum*, since such a state of affairs could only exist when the Planck oscillators are entirely independent of each other, as would be the case if we were considering the molecules of a gas. It is a fundamental aspect of the crystalline state that the oscillators of which it is composed are coupled to each other more or less firmly. In diamond, for example, the bonds connecting the different lattice cells with each other are exactly of the same kind as those

which bind the atoms within the cell. The proposition that the internal oscillations occurring in the neighbouring cells of the lattice are uncorrelated in phase is thus entirely indefensible. Indeed, it would be more reasonable to make exactly the contrary assumption, namely that the phases of the oscillations in neighbouring cells are so highly correlated with each other that to all intents and purposes, the entire piece of diamond functions as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency. Only on some such view could we hope to understand the extraordinarily perfect monochromatism of the lattice vibrations in diamond.

We may summarise the situation by stating that the Born postulate does not represent the true state of affairs in a crystal except in regard to the low-frequency elastic vibrations, in which case, of course, it is of no particular significance. The real state of affairs in a crystal demands that if the distribution of phase of the Planck oscillators in a specified volume could be represented as a three-dimensional Fourier series, only the terms which have wave-lengths large compared with the lattice spacings and orientations specifically related to the geometry of the crystal structure would be allowed, while terms with phase wave-lengths of the same order as the lattice spacings would be altogether excluded. The stronger the atomic forces and the tighter the resultant mechanical coupling between the lattice cells, the more nearly would we approach a state of affairs in which the entire crystal behaves as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency.

6. *Fundamental Defects of the Existing Theories*

Born's postulate of the cyclic lattice which has been discussed in the foregoing pages and shown to be untenable was the basis on which Debye, Waller and Laue developed their treatments of the problem of the temperature effect in X-ray diffraction. It follows that, quite apart from the incompetence of the classical mechanics to deal correctly with the problem, these earlier investigations were also otherwise fundamentally defective, being in fact based on an erroneous conception of the nature of the vibrations in a crystal lattice. The picture of the X-ray phenomena which they present differs radically from the truth, failing as it does to indicate the fundamental difference between the low-frequency or continuous spectrum of elastic vibrations and the high-frequency or monochromatic vibrations in the infra-red, in respect of the X-ray effects to which they give rise. This is not surprising as the theories start from the assumption that these modes of vibration are essentially similar.

To make the foregoing points clear, we proceed to show from first principles how essentially the X-ray effects due to these two types of vibration of the lattice must differ. We shall consider first the elastic vibrations of the crystal lattice. These involve translatory movements of the lattice cells of the crystal from their positions of equilibrium. It is evident that if there are N lattice cells in the crystal, such translations would involve 3 N degrees of freedom. They may therefore be regarded as due to the superposition of 3 N sets of elastic waves of all the possible wave-lengths and frequencies, these having equal weight. It follows that the movements of any individual cell resulting from such superposition would be uncorrelated with that of any other lattice cell in the crystal. Hence, the secondary radiations of modified frequency sent out from the individual cells would be incoherent. In other words, the elastic vibrations would result in a secondary radiation of which the aggregate intensity is proportional to the number of lattice cells and which is in the nature of a diffuse or scattered radiation. This argument is not invalidated by the fact that the oscillation of a *particular* frequency expressed by one of the terms in the Fourier representation has a specifiable phase-relation in respect of the different lattice cells. The contradiction disappears when we remember that the number of degrees of freedom allotted to a *particular* frequency in a continuous spectrum is only one out of the very large number N. Hence, in spite of the fact that an elastic vibration of a specified frequency may be considered to be a coherent type of oscillation, the effect of all such vibrations taken together is essentially an incoherent radiation or diffuse scattering of which the intensity is proportional to N the number of lattice cells and not to N^2.

The position is entirely different when we consider the monochromatic vibrations of the lattice cells. The monochromatism implies that all the N degrees of freedom refer to a single mode of oscillation, which in the limiting case is pictured as having identically the same frequency, amplitude and phase in all the lattice cells of the crystal. The movements of the atoms within a cell results in secondary radiations from the atoms, and therefore also from the cells, possessing components of modified frequency. The identity of the oscillation in all the lattice cells ensures that these secondary radiations received at any external point have coherent phase-relationships. Hence, these are capable, exactly as in the case of the secondary radiations of unmodified frequency, of giving rise to interference effects. Indeed, it is clear that they would result in a *geometric reflection of the X-rays by the lattice planes of the crystal but with modified frequency.* In the limiting case when all the cells vibrate in identical phase, the direction in

which this modified geometric reflection would appear is the same as that of unmodified reflection.

We thus see that the elastic vibrations of the solid and the infra-red vibrations of the lattice cells give rise to X-ray effects which are fundamentally different and which, in fact, portray in a geometric form the radically different spectroscopic characters of the two modes of vibration. The elastic vibrations give a diffuse scattering of the incident X-rays with an intensity proportional to N, the number of lattice cells, while the infra-red vibrations give geometric reflections of altered frequency of which the intensity (subject to the same limitations as in the case of the unmodified reflections) is proportional to N^2. It will be noticed that these results are consequential on our rejection of the Born postulate. Had the latter been valid, both types of vibration would have given a diffuse scattering proportional to N, the number of lattice cells; this, in fact, is the result emerging from the investigations of Debye, Waller and Laue, except that the actual result due to the elastic vibrations appears exaggerated in their papers by the assignment to them of $3p$ N degrees of freedom instead of 3 N the correct number, p being the number of atoms in the unit cell of the lattice. That the internal vibrations within the lattice cells are not considered at all is clear from Laue's memoir where the positions of the atoms within the unit cell are explicitly regarded as constants.

7. *Quantum Reflection of X-Rays*

The preceding discussion enables us to proceed further and give a quantitative picture of the geometric reflection of X-rays by the lattice planes of a crystal with altered frequency. We consider the individual cells of the crystal lattice as Planck oscillators of frequency ν^*, so that, when excited, the energy of each oscillator is $h\nu^*$. An oscillation with this energy would result in the atoms in the cell being set in vibration such that the sum total of their kinetic energies in passing through the position of equilibrium is equal to $h\nu^*$. We then write down the expressions for the secondary radiations of various frequencies from each of the atoms in the cell. These are then summed up in the usual way, taking the positions of the atoms into account, to find the structure factor of the lattice cell. *This is done separately for each of the different frequencies of secondary radiation.* If the frequency ν^* is sufficiently high in relation to the temperature of the crystal, in other words, if $h\nu^* \gg kT$, it is sufficient to consider only the component having the primary or unmodified frequency ν and the component with diminished frequency $(\nu - \nu^*)$. Assuming that the setting of the crystal is such that the Laue conditions are satisfied for a particular set of lattice

planes, it would follow that the primary X-rays of frequency ν would then be reflected by these planes. Simultaneously, the modified radiations of frequency $(\nu - \nu^*)$ would also be reflected by the same planes and in the same direction, provided we assume that the phase of the vibration of frequency ν^* is the same for all the cells in the crystal. The intensity of the modified reflection of frequency $(\nu - \nu^*)$ would be determined by the dynamic structure factor of the lattice cell, in exactly the same way that the intensity of the unmodified reflection of frequency ν is determined by the static structure factor.

It will be noticed that this argument assumes that each of the N cells of the lattice is excited with an energy $h\nu^*$. It might seem at first sight that this would involve the entire crystal abstracting an energy $Nh\nu^*$ from the energy $h\nu$ of the incident X-ray photon, which of course, is impossible, besides being inconsistent with the assumed frequency $(\nu - \nu^*)$ of the reflection. Actually, all that the argument assumes is that the crystal functions as a single oscillator of frequency ν^* but with a statistical weight N times greater than that of a single lattice cell. This of course is only possible when all the cells vibrate in identically the same way, as is actually assumed in the argument. The intensity of the reflection calculated in this way would be the maximum possible. It may be regarded as an estimate of intensity to be expected in the most favourable setting of the crystal, *viz.*, when the Laue conditions are satisfied also for the unmodified reflection. It may be emphasized that the quantum reflection is the result of a transition of the crystal from the ground state to a higher energy level of vibration, the energy required for the transition being derived from the incident radiations themselves and not from the energy of the thermal agitation of the crystal. Indeed in the circumstances considered, namely when $h\nu^* \gg k\mathrm{T}$, thermal agitation is non-existent and can therefore play no part in the phenomenon. It may be remarked also that the so-called zero point energy which finds a place in the earlier semi-classical investigations of the X-ray problem becomes irrelevant from our present point of view.

8. *Quantum Scattering of X-Rays*

We now proceed to consider the X-ray effects arising from the elastic or low-frequency vibrations of the crystal lattice. As already remarked, these vibrations displace the lattice cells as a whole from their positions of equilibrium. Considering an elastic vibration of a particular wave-length, we notice that the stratifications in the medium arising from it are of two distinct kinds. Firstly, the elastic wave may itself, if it be of the longitudinal type, be regarded as a periodic stratification of electron density in a medium

which may otherwise be considered as uniform. This view of the matter is appropriate when we are concerned with stratifications with a spacing greater than the largest grating intervals in the crystal. Secondly, the elastic waves, more particularly those of the transverse type, disturb the regular arrangement of the lattice cells, so that the structure amplitudes of the crystal plane are diminished and, *per contra*, new dynamic stratifications are created due to the superposition of the elastic waves and the static crystal planes. This is the point of view developed in detail in Laue's memoir. The scattering of the X-rays by either of the processes indicated would necessarily involve a change of frequency. The scattering by the elastic waves themselves would appear in directions making smaller angles with the primary X-ray beam (assumed to be monochromatic) than the scattering due to their combinations with the crystal spacings. The two effects together give the background or diffuse scattering of X-rays by the crystal.

Since the elastic vibrations are of relatively low frequency, the situation may be represented in the majority of such cases by the inequality $h\nu^* \ll k\mathrm{T}$, ν^* being the frequency of elastic vibration. When this is the case, the results to be expected from the classical and quantum theories would be identical. In other words, the effects observed may be described as the result of each of the elastic modes of vibration possessing an energy $k\mathrm{T}$, the scattered radiations appearing with equal intensity in the two frequencies $(\nu \pm \nu^*)$. It must not be assumed, however, that a treatment on these lines would represent the facts of X-ray scattering in every case. Whenever the elastic frequency ν^* under consideration is high or the temperature T of the crystal is low so that $h\nu^* \gg k\mathrm{T}$, the situation would be reversed. The intensity of X-ray scattering would then be the result of assigning an energy $h\nu^*$ to each vibration, and it follows that it would then be much greater than that given by the classical considerations. Since the energy is abstracted from the incident quantum, the scattered radiation would then appear only with diminished frequency $(\nu - \nu^*)$. It is evident also that the semi-classical considerations based on the Planck specific heat formula and the existence of zero point energy of the kind which figure in the earlier X-ray investigations cannot describe the situation correctly and are therefore irrelevant.

9. *Characters of the Two Effects*

It is evident from the foregoing discussion that the effects arising respectively from the vibrations in the infra-red and the elastic ranges of frequency are entirely different. Numerous criteria present themselves which make it possible to distinguish the one from the other.

Firstly.—The geometric distribution of the secondary X-radiations is widely different in the two cases, being a regular reflection of the incident X-rays by the lattice planes in one case and a diffuse scattering in the other. The influence of the setting of the crystal on the two phenomena is determined by considerations of a wholly distinct kind and should therefore also be quite different.

Secondly.—The intensity in one case is proportional to N^2, *viz*., the square of the number of effective lattice cells and in the other case to N. Variations of the thickness of the crystal plate and of the cross-section of the X-ray beam traversing it would therefore influence the two phenomena in entirely different ways.

Thirdly.—The dynamic structure amplitudes for the quantum reflections are determined by the modes of atomic vibration and are not necessarily proportional to the static structure amplitudes. It is quite possible, for instance, that the dynamic structure amplitude for a particular set of crystal planes is zero while the static structure amplitude for the same planes is finite, or *vice versa*. In other words, the intensities of the classical and quantum reflections by any given set of crystal planes are not necessarily proportional to each other. Such a situation cannot rise in the quantum scattering of the X-rays, as this is due to the simple translatory movements of the lattice cells.

Fourthly.—Since the two phenomena arise from vibrations of the crystal lattice lying in widely different ranges of frequency, their intensity variations with temperature would be markedly different. In either case, a finite limiting intensity would be reached at low temperatures, but this would be far greater relatively to the intensity at ordinary temperatures for the infra-red vibrations than for the elastic ones.

Fifthly.—The characters of the quantum reflections and their variation with physical conditions such as temperature should exhibit a close correlation with the spectroscopic behaviour of the substance in the infra-red region; the quantum scattering, on the other hand, should show a correlation with the elastic behaviour of the substance.

Sixthly.—The changes of frequency, if directly observable, would naturally be much greater for the quantum reflections than for the quantum scattering.

10. Summary

The paper examines the views generally current at the present time regarding the nature of the vibrations possible in a crystal lattice which

are based largely on the specific heat theory of Debye and the crystal dynamics of Max Born and his school. The latter has for its starting point the so-called postulate of the "cyclic lattice". It is here shown that this postulate is an *ad hoc* supposition adopted for mathematical convenience and that, far from being justifiable, its consequences are definitely contradicted by the known spectroscopic behaviour of crystals and that it is also contrary to the dynamic behaviour which should be expected from a set of coupled Planck oscillators such as the lattice cells of a crystal constitute. It is also shown that the modes of vibration of the elastic type forming a continuous spectrum and the modes of vibration having discrete or monochromatic frequencies in the infra-red region have fundamentally different dynamic characters. Starting from the proposition established by Laue that the secondary X-radiation from an oscillating atom exhibits components of modified frequency, it is shown how the resultant effects of the secondary radiations of modified frequency due respectively to these two types of vibration can be evaluated. It is shown further that the infra-red vibrations result in geometric reflections by the lattice planes of the crystal but with altered frequency, their intensity (subject to the same limitations as for the classical reflections) being proportional to N^2, that is, to the square of the number of lattice cells in the crystal. On the other hand, the elastic vibrations of low frequency give a diffuse scattering of the X-rays of which the intensity is proportional to N. As both these effects involve changes of frequency, the classical mechanics is incompetent to describe them correctly, and has therefore to be replaced by quantum-mechanical considerations. It is shown how this can be done quantitatively. The temperature dependence of both these effects is discussed. Finally, numerous experimental criteria are presented distinguishing the two effects which should prevent them from being mistaken for each other.

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QUANTUM THEORY OF X-RAY REFLECTION: MATHEMATICAL FORMULATION

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1. Introduction

As was pointed out by Laue (1926), the secondary radiations from the atoms in a crystal traversed by a monochromatic beam of X-rays suffer changes of frequency when the atoms oscillate about their positions of equilibrium. These changes of frequency play a fundamental rôle in determining the observed X-ray phenomena. For, the superposition of radiations which differ in frequency cannot give rise to observable interferences, while, on the other hand, secondary radiations of identical frequency are necessarily coherent and capable of interfering with each other even if the frequency differs from the primary X-ray frequency. Accordingly, if we fix our attention on a particular mode of vibration of the atoms in a crystal, the radiations of altered frequency arising therefrom can give rise to interference maxima in just the same way as the radiations from stationary atoms. It follows also, that if several vibrations co-exist in a crystal, each set of secondary radiations of different frequency thus arising would produce its own interference maxima independently of the others. If, further, the individual vibrations are of infinitesimal amplitude, a considerable simplification becomes possible. For, then each vibration may be regarded as giving rise to its own secondary radiations and acting independently of all the others, provided its frequency is different from theirs. This statement, however, requires some qualification when the excursions of the atoms about their positions of equilibrium

resulting from the totality of all the vibrations present have a finite amplitude. For, the total radiation amplitude of an atom is fixed and is equal to the superposed radiation amplitudes of various frequencies. Hence, the radiation amplitude due to any particular vibration frequency would naturally be less than it would be in the absence of all the others. It is evident also that as the atomic excursions increase, the strength of the secondary radiations of the original or primary X-ray frequency and of the interference maxima to which they give rise must progressively diminish, finally tending to zero.

The elastic or low-frequency modes of vibration have a continuous spectrum of frequencies and hence, as explained above, the optical effects of each vibration should be considered separately. Since the energy corresponding to a particular frequency is small and is further distributed over all the atoms in the crystal, the resulting atomic amplitudes are exceedingly small. Hence, the secondary radiations due to these separate vibrations are exceedingly weak, and since they are incoherent, their intensities and not their amplitudes should be added. In the final result, therefore, we have an effect which is inherently feeble and which can only become important when a large volume of the crystal is under consideration.

The position is different when we consider the effect of modes of vibration of the crystal which appear as monochromatic frequencies in its infra-red spectrum. Each such line in the spectrum represents N co-existent modes of vibration, where N is the number of the lattice cells in the crystal. In the ideal case when all the N modes are of identical frequency, it is evident that the secondary radiations of altered frequency due to these co-existing modes would all be coherent and must therefore be considered *together* and *not separately*. It is evident, therefore, that the vibrations of the infra-red type can give rise to effects of an altogether higher order of intensity than the elastic vibrations considered above. This result has already been deduced in an earlier paper from a consideration of the phase relations subsisting between the lattice cells in a crystal in an infra-red vibration. Its possibility, it may be remarked, is consequential on our rejection of the ideas of Debye and Born regarding the nature of the high frequency vibrations in a crystal lattice, and especially of the so-called postulate of the "cyclic lattice" due to Born which we have considered in detail and shown to be untenable.

It should be noted that the elastic and infra-red modes of vibration of a crystal also differ in other respects. In the former case, the basic grouping of the atoms in the lattice cells remains unaltered, while in the latter, it is to be regarded as essentially a variable. Then again, the wave-fronts of an elastic vibration may have any possible orientation within the crystal, while for the infra-red vibrations, there is *prima facie* no reason for assuming that this

should be the case. It has also to be remembered that the elastic vibrations are of lower frequency than the infra-red ones; this makes a considerable difference in considering the influence of thermal agitation in the two cases.

As already explained in the preceding paper, the recognition of the changes of frequency, the importance of which was first emphasised by Laue, leads us naturally to bring the X-ray problem within the scope of the quantum theory of radiation. It also makes the transition from the classical to the quantum mechanical considerations very simple. The changes of frequency indicated by the classical electrodynamics appear in the quantum theory as the result of exchanges of energy between the quantum and the crystal lattice. Similarly, the Laue conditions for a dynamic reflection are the same as those required for the conservation of momentum in the encounter between the quantum and the crystal. The principal difference between the classical and quantum points of view is in regard to the question of the absolute intensity of the secondary radiations and its dependence on temperature. Here, the quantum mechanical considerations replace such incorrect applications of the quantum theory to X-ray physics as are usually made by introducing the Planck factor and the zero point energy, neither of which is really relevant when considering the exchanges of energy betwen matter and radiation.

2. *Secondary Radiations from an Oscillating Atom*

Under the influence of waves of unit amplitude, an atom emits secondary radiations which at a distance R from the origin of co-ordinates and in a direction making an angle 2ψ with the primary ray have the amplitude

$$f \sin \beta \cdot \frac{e^2}{mc^2} \cdot \frac{1}{R} \cos 2\pi \left(\nu t - \frac{R + 2\,D \sin \psi}{\lambda} \right), \tag{1}$$

where D is the perpendicular distance of the atom from a reference plane through the origin bisecting the angle between the primary and secondary rays, f is the atomic structure factor, and β the angle between the electric vector in the incident pencil and the diffracted ray. It is evident that this expression would remain invariable if the atom moves parallel to the reference plane but would alter periodically if it oscillates perpendicular to it. Writing

$$D = d + a \cos (2\pi \nu^* t + z) \tag{2}$$

the periodic part of (1) may be written as

$$\cos [2\pi \nu t - Z - \zeta \cos (2\pi \nu^* t + z)] \tag{3}$$

where

$$Z = \frac{2\pi (R + 2d \sin \psi)}{\lambda}, \quad \zeta = \frac{4\pi a \sin \psi}{\lambda}. \tag{4}$$

The expression (3) may be expanded in a series of Bessel functions. Neglecting

the functions of higher order than the first, it may be written as

$$J_0(\zeta)\cos(2\pi\nu t - Z) + J_1(\zeta)\sin[2\pi(\nu \pm \nu^*)t - Z \pm z]. \quad (5)$$

The three quantities Z, ζ and z appearing in (5) are all phase angles. Z is the phase of the secondary radiation from the atom when it is in the position of equilibrium, ζ the change of this phase produced by displacing the atom through a distance α in a direction normal to the reference plane, and z is the phase of the atomic vibration. Expression (5) indicates that the secondary radiation from the oscillating atom consists of three components whose amplitudes depend on the amplitude of the oscillation and which differ in frequency and phase. The first component has the frequency ν of the primary X-rays and its phase is determined solely by the equilibrium position of the atom. Its amplitude has however been diminished by the movement of the atom in the ratio $J_0(\zeta):1$. The second and third components have the same amplitude, namely $J_1(\zeta)$, but they differ in frequency and phase. The component $(\nu+\nu^*)$ has a phase angle $(Z-z)$, while the component $(\nu-\nu^*)$ has a phase angle $(Z+z)$. The secondary radiations of altered frequency thus increase in amplitude with increasing vigour of the atomic vibration, while their phases are determined jointly by the atomic positions and the phase of the atomic vibrations. The equality of the amplitudes of the components of increased and diminished frequency indicated by (5) is a typical consequence of the classical electrodynamics which will later be amended in the light of quantum mechanics.

3. *Dynamic Stratifications of Density*

We may now proceed to deduce the optical effect of all the atoms vibrating with the same frequency but with a phase which may be assumed to vary slowly from place to place within the crystal. For the purpose of a graphical derivation of the conditions for interference, it is not necessary at the present stage to distinguish between the elastic and infra-red modes of vibration. We consider a particular set of lattice planes in the crystal marked *d d d* in the figure.

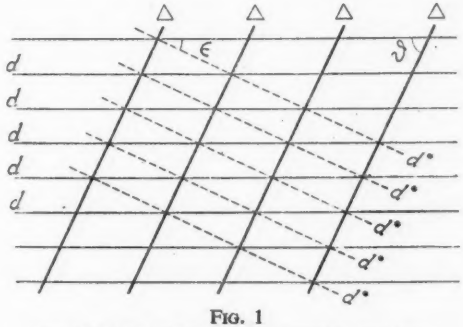

FIG. 1
Graphical Derivation of the Dynamic Spacings

It is evident that for any given setting of the crystal the phase of the secondary radiations as received at a distance will vary from point to point within the crystal. In respect of the secondary radiations of unmodified frequency, this phase is given by Z. Hence, to obtain the maximum resultant intensity, Z must be invariable along a crystal plane and jump by 2π or an integral multiple thereof, as we pass from plane to plane. In other words, the planes $d\,d\,d$ should make equal angles with the incident and diffracted rays, and their spacing d should satisfy the relation

$$2\,d \sin \theta_c = \lambda. \tag{6}$$

This is the familiar optical formula for a monochromatic reflection from a regularly stratified medium. θ_c indicates the glancing angle for a classical or unmodified reflection.

Considering now the secondary radiations of altered frequency, we see that their resultant is determined by the variation of $(Z - z)$ in one case and of $(Z + z)$ in the other. Let $\Delta\,\Delta\,\Delta$ in the figure represent the planes along which the phases of the atomic vibrations, in other words the values of z, are constant. In order to obtain the maximum intensity for the resultant of the secondary radiations, the crystal should be so set that $(Z - z)$ or $(Z + z)$ as the case may be, is constant along the lattice planes ; it is evident from the figure that this would be the case if the setting of the crystal is such that the incident and diffracted rays are equally inclined to the planes which run diagonally cutting the $d\,d\,d$ and $\Delta\,\Delta\,\Delta$ planes, *e.g.*, $d^*d^*d^*$ as shown in Fig. 1. For obtaining the maximum intensity, a further condition must be satisfied, namely

$$2d^* \sin \psi = \lambda, \tag{7}$$

where ψ is, as before, half the angle between the incident and diffracted rays. It is evident from the figure that there are two sets of diagonal planes possible. But the same set will satisfy equation (7) for both the frequency components $(\nu + \nu^*)$ and $(\nu - \nu^*)$, provided that we assume the phase angle Z advances in one case and recedes in the other case as we move across the figure. The diagonal planes $d^*\,d^*\,d^*$ thus represent the dynamic stratifications of electronic density resulting from the vibrations of the atoms contained in the lattice planes of the crystal. As the phase waves $\Delta\,\Delta\,\Delta$ move from left to right, the dynamic stratifications $d^*d^*d^*$ move upwards, keeping a constant spacing, while if the phase waves $\Delta\,\Delta\,\Delta$ move from right to left, the spacings $d^*d^*d^*$ move downwards in the same way. The changes of frequency from ν to $(\nu \pm \nu^*)$ may thus be regarded as analogous to the Doppler effect in the reflection from a moving mirror.

4. *Geometric Law of Dynamic Reflection*

The spacing d^* of the dynamic statifications is connected with the spacing d of the static ones and the phase-wave length Δ of the atomic vibrations by the vectorial relation,

$$\frac{\vec{1}}{d^*}=\frac{\vec{1}}{d}+\frac{\vec{1}}{\Delta}. \tag{8}$$

This is readily deduced by writing down the vectorial equation represented by the three sides of one of the triangles appearing in Fig. 1 and dividing the same by the area of the triangle. Denoting by ϑ the angle between the planes $d\,d\,d$ and the phase waves $\Delta\,\Delta\,\Delta$, and by ϵ the angle between the planes $d\,d\,d$ and $d^*d^*d^*$, we have from Fig. 1 and equation (8)

$$d^* \sin \vartheta = d \sin (\vartheta \pm \epsilon) = \Delta \sin \epsilon. \tag{9}$$

Substituting the first of these relations in (7), we obtain

$$2\,d \sin \psi \sin (\vartheta \pm \epsilon) = \lambda \sin \vartheta. \tag{10}$$

Equation (10) is the general geometric law of dynamic reflection deduced by Raman and Nath (1940). It will be noticed from (9) that when the phase wave-length Δ is infinite, $\epsilon = 0$ and $d^* = d$, from which it follows that $\psi = \theta_c$. In other words, the static and dynamic reflections then coincide in direction. This is also obvious directly from Fig. 1. In general, however, d^* and d are different, and the conditions for the possibility of static and dynamic reflections are not the same. While a static reflection can only occur at the particular setting of the crystal indicated by (6), a dynamic reflection is evidently possible over a wide range of settings of the crystal determined by the permissible values of the phase wave-length Δ. It is further to be remarked that while the glancing angles of incidence and reflection are equal for the static reflections given by (6), these angles when measured as usual with reference to the static crystal planes would generally differ from each other for the dynamic reflections. Further, the latter reflections would in general appear in a plane different from that of the incidence of the X-rays on the crystal spacings. To specify the actual plane of dynamic reflection, it is necessary to know the angle χ which determines the azimuth of the phase waves. We may put $\chi = 0$ in the case when the dynamic reflection appears in the plane of incidence, the phase waves then being evidently perpendicular to that plane. When $\chi \neq 0$, the dynamic reflection swings out of the plane of incidence to an extent determined by the values of Δ, ϑ and χ.

In the particular case when $\chi = 0$, it is evident that

$$\phi + \theta = 2\,\psi, \text{ and that } \phi - \theta = 2\epsilon, \tag{11}$$

where θ and ϕ are respectively the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Equation (10) may then be written as

$$2\,d \sin\frac{\theta+\phi}{2} \sin\left(\vartheta \pm \frac{\theta-\phi}{2}\right) = \lambda \sin\vartheta. \tag{12}$$

The value of ϕ then depends on the angle ϑ. If we imagine ϑ to march from 0 to π, equation (12) shows that the relation between ϕ and θ will alter from

$$\phi = \theta, \text{ when } \vartheta = 0 \text{ or } \pi \tag{13}$$

to

$$d\,(\sin\theta + \sin\phi) = \lambda, \text{ when } \vartheta = \frac{\pi}{2}. \tag{14}$$

Thus, when the phase waves are *parallel* to the crystal planes, the dynamic reflection always satisfies the ordinary geometric law of reflection from the crystal planes, while if the phase waves are transverse to the crystal planes, it appears in the direction given by (14) which may be written *approximately* as

$$2\,d \sin\frac{\theta+\phi}{2} = \lambda \tag{15}$$

thereby indicating that the angle between the incident and reflected rays is approximately constant and independent of the crystal setting.

5. *Dynamic Structure Factor*

To find the conjoint effect of the secondary radiations from all the atoms in the unit cell of the lattice, we have to sum them up considering each component of frequency separately. This summation for the radiations having the primary X-ray frequency gives (omitting constant factors),

$$\Sigma_p f_p\, J_0(\zeta_p) \cos(2\pi\nu t - Z_p). \tag{16}$$

The summation for the secondary radiations of frequency $(\nu \pm \nu^*)$ similarly gives

$$\Sigma_p f_p'\, J_1(\zeta_p') \sin[2\pi(\nu \pm \nu^*)\, t - Z_p' \pm z_p'] \tag{17}$$

the index p referring to the pth atom in the cell, and the dashes in (17) indicating that the setting of the crystal and the angle of diffraction are not necessarily the same as those considered in (16). Remembering, however, the conditions for a dynamic reflection discussed in the foregoing section, namely that $Z \pm z$ should be constant along any particular lattice plane, we may simplify (17) and write it in the form

$$\Sigma_p f_p'\, J_1(\zeta_p') \sin[2\pi(\nu \pm \nu^*)\, t - Z_p] \tag{18}$$

Z_p having now the same significance as in (16) for a static reflection by the same set of lattice planes. A further simplification arises when the angle between the primary and diffracted radiations does not differ greatly for (16) and (18). We may then write, approximately, $f_p' = f_p$. If, further, the setting of the crystal in the two cases is not so greatly different, we may also write, $\zeta_p' = \zeta_p$, as an approximation. Subject to the restrictions indicated, (17) now takes the form

$$\sum_p f_p \, J_1(\zeta_p) \cdot \sin [2\pi(\nu \pm \nu^*) t - Z_p]. \tag{19}$$

The static structure factor of the unit cell as influenced by the particular vibration may therefore be evaluated by diminishing the structure factor of each atom in the ratio $J_0(\zeta_p)$ to unity. At the same time, the lattice cell acquires a dynamic structure factor which is found in exactly the same way except that the structure factor of each atom is now multiplied by $J_1(\zeta_p)$.

Very significant differences now arise in considering respectively the elastic and the infra-red vibrations. For the elastic vibrations, ζ_p is the same for all the atoms in the unit cell. The suffix p may therefore be removed and the Bessel functions taken outside the summation sign. For an elastic vibration, therefore, the static and dynamic reflections may be evaluated from the expressions

$$J_0(\zeta) \cdot \sum_p f_p \cdot \cos(2\pi \nu t - Z_p) \tag{20}$$

$$J_1(\zeta) \cdot \sum_p f_p \cdot \sin [2\pi(\nu \pm \nu^*) t - Z_p]. \tag{21}$$

The static and dynamic structure factors in the case of an elastic vibration thus differ only by a multiplying factor which is the same for all the atoms in the unit cell. Thus, if a particular set of crystal planes gives zero intensity for a particular order of reflection, the dynamic reflections for the same planes and the same order of reflection must also vanish. The dynamic reflections by different sets of crystal planes would follow the same order of intensity as the static reflections by those planes, provided the amplitude of the elastic vibrations transverse to the planes may be assumed to be the same. A similar remark would also apply to the relative intensities of the successive orders of reflection by a particular set of planes, except that the factor $J_0(\zeta)$ diminishes while the factor $J_1(\zeta)$ increases as the angle of diffraction becomes larger, *vide* equation (4).

The position is greatly altered when we consider the infra-red vibrations of the lattice. Here, the displacements being different for the different atoms, the factors $J_0(\zeta_p)$ and $J_1(\zeta_p)$ must remain within the summation signs. Some of the atoms in the lattice cell must evidently move in directions opposite to

the others if the centre of gravity of the cell is to remain undisplaced. Hence $J_1(\zeta_\rho)$ would be positive for some of the atoms and negative for the others in an infra-red vibration, while on the other hand $J_0(\zeta_\rho)$ would always be positive and nearly equal to unity. It follows that the static and dynamic structure factors for an infra-red vibration are determined by quite different considerations and cannot, in general, exhibit the close parallelism indicated by the theory for the elastic vibrations. Indeed, it may well happen that in particular cases, the static structure factor vanishes while the dynamic structure factor remains finite, or *vice versa*.

6. *Quantum Scattering by Elastic Vibrations*

The disturbance produced by an elastic vibration on X-ray propagation is of two kinds. Firstly, a compressional wave would evidently alter the average electronic density. It is thus itself a dynamic stratification of the medium capable of reflecting the X-rays with a frequency $(\nu \pm \nu^*)$, increased or decreased as the case may be, depending on the direction of the wave. Such a reflection occurs when

$$2\Delta \sin\psi = \lambda, \tag{22}$$

large values of Δ corresponding to small values of ψ, and *vice versa*. Thus, since Δ may have any one of a practically continuous series of values determined by the dimensions of the crystal, and since the orientation of the wave is arbitrary, the reflection indicated by equation (22) would result in a cone of scattered X-rays (the Brillouin cone) having the direction of the primary beam as its axis. The angular extension of the cone depends on the smallest permissible values of Δ. The intensity of such scattering would depend on the energy of the vibration and the resulting variation of electron density. On the classical mechanics, the energy of an elastic vibration of thermal origin may be taken as KT, while if the wave is quantum-mechanically excited by the incident radiation, the energy would be $h\nu^*$. The latter assumption would be the appropriate one to make if $h\nu^* \gg$ KT, while if $h\nu^* \ll$ KT, the former assumption would be correct. This type of X-ray scattering should therefore be exhibited by crystals even at the lowest temperatures and in the absence of thermal agitation, and especially by crystals of high elasticity, *e.g.*, diamond. We should expect the intensity of the X-ray scattering by such crystals to be greater than that indicated by the classical considerations even at ordinary temperatures.

The second kind of disturbance to X-ray propagation arises from the distortions which the elastic waves cause to the regular stratifications of the crystal structure. The formulæ of the three preceding sections enable us to evaluate these effects quantitatively in a very simple manner. As explained

in Section 3 and illustrated in Fig. 1, the superposition of an elastic vibration on a specified set of crystal planes gives rise to dynamic stratifications of density. As further explained in Section 4, these stratifications reflect the incident X-rays in the direction given by the general geometric law (10). The intensity of such reflection is determined by the dynamic structure factor as explained in Section 5.

Considering the *direction* in which the so-called dynamic reflection appears, it is evident from equations (9) and (10) that this depends on the wave-length Δ, the angle ϑ which the wave-fronts make with the crystal spacings, and also upon the azimuth χ of the wave-fronts. A variation of χ would throw the dynamic reflection out of the plane of incidence, while if $\chi = 0$, the reflection would appear in that plane. A dynamic reflection is only possible when the X-ray wave-length, the dynamic spacing d^* and the glancing angle ψ of incidence of the X-rays thereon are suitably related. But since we have at our disposal two variables, namely Δ and ϑ, we may, as is evident from Fig. 1, by suitably altering both of them get a dynamic reflection *in any desired direction. In other words, the resultant effect of all the elastic vibrations is a diffuse scattering of the X-rays over a wide range of solid angles* and not a geometric reflection in any specified direction.

To find the X-ray scattering due to any particular set of crystal planes, we have only to evaluate the two expressions (20) and (21) given previously. Their magnitudes are in the ratio $J_0(\xi) : J_1(\zeta)$. If ζ be sufficiently small, $J_0(\zeta)$ is practically unity while $J_1(\zeta)$ would be equal to $\frac{1}{2}\zeta$. If m be the mass of an unit cell of the lattice, the energy of vibration of N such cells, each having an amplitude α with a frequency ν^* would be $2\pi^2\, m\mathrm{N}\alpha^2\nu^{*2}$. This may be written in the form $2\pi^2 \cdot \mathrm{M}\sigma^2 \cdot \alpha^2/\Delta^2$, where M is the mass of the whole crystal, σ is the velocity of the elastic waves and Δ is their wave-length. Utilising equations (4), (7) and (9), we may write this in the simple form

$$\tfrac{1}{2}\zeta^2 \cdot \mathrm{M}\sigma^2 \cdot \sin^2\epsilon/\sin^2\vartheta. \tag{23}$$

This may now be put equal to KT (classical mechanics). Accordingly, we have

$$\tfrac{1}{2}\zeta^2 = \mathrm{KT}/\mathrm{M}\sigma^2 \cdot \sin^2\vartheta/\sin^2\epsilon. \tag{24}$$

Equation (24) gives the ratio of the sum of the squares of the dynamic structure factors to the square of the static structure factor. It is evidently of the order $1/\mathrm{N}$ and is thus an exceedingly small quantity. The X-ray scattering in any specified direction due to the distortion of the crystal planes by the elastic waves is therefore of vanishingly small intensity in comparison with the intensity of regular reflection by the same crystal planes and should be unobservable except when relatively large volumes of the crystal are under consideration.

The numerical factor $\sin^2\vartheta/\sin^2\epsilon$ appearing in equation (24) determines the manner in which the intensity of the scattered radiation varies with direction. It may be written also as Δ^2/d^{*2}, where Δ and d^* have the same significance as in equation (8). Thus the intensity of the scattering would be greatest in those directions for which the wave-length Δ of the elastic waves which effectively scatter the X-rays is greatest. This variation arises because the amplitude of the elastic waves is directly proportional to their wave-length, and the scattering is therefore greatest in the directions in which the waves of longest wave-length and lowest frequency are effective. The nature of the variation can be readily made out from Fig. 2, which represents the geometric relation between $1/d$, $1/d^*$ and $1/\Delta$ given by equation (8), as also the relation between $1/d^*$, $1/\lambda$ and $\sin\psi$ expressed by equation (7).

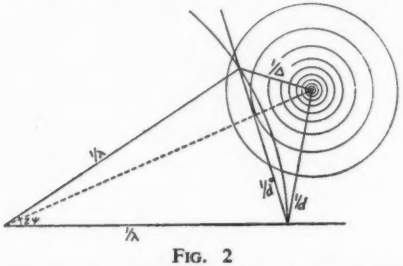

FIG. 2

Distribution of Intensity of Diffuse X-Ray Scattering

Spheres are drawn (sections of which by the plane of the figure appear as circles) round the terminus of the vector $1/d$ and with radii $1/\Delta$; points on the spheres represent various values and orientations of the vector $1/\Delta$ drawn from their common centre. The spheres are drawn closely together near their centre and further away at a distance from it to suggest the rapid diminution of the amplitude of the elastic waves with diminishing wave-length. A sphere of reflection is drawn with radius $1/\lambda$ around O as centre. It cuts across the " spheres of diffusion " having the radii $1/\Delta$ and the scattered radiations would therefore appear over the entire area of the sphere of reflection thus cut by the spheres of diffusion. When the sphere of reflection actually passes through the terminus of the vector $1/d$, the maximum of scattering intensity would fall on the sphere itself, but as it would then coincide with the regular reflection, the maximum would be unobservable. In other cases, the scattering would show a very broad and diffuse maximum of intensity corresponding to the minimum value of $1/\Delta$ on the sphere of reflection. This maximum however becomes rapidly weaker and more diffuse as the sphere of reflection passes further away from the centre of the spheres of diffusion with altered settings of

the vector $1/d$. *Hence, nothing even remotely resembling a regular geometric reflection which persists over a wide range of settings of the crystal would be exhibited by the X-ray scattering due to the elastic waves.*

The same situation can be represented graphically by plotting the function $\sin^2\vartheta/\sin^2\epsilon$ for various settings of the crystal. It is sufficient if this is done for the scattered radiations lying in the plane of incidence. With the aid of the formulæ (6), (7), (9) and (11), it is readily shown that

$$\frac{\sin^2\vartheta}{\sin^2\epsilon} = \frac{\sin^2(\theta+\epsilon)}{\sin^2\theta_c - 2\sin\theta_c \sin(\theta+\epsilon)\cos\epsilon + \sin^2(\theta+\epsilon)}. \tag{25}$$

It is seen on differentiating the denominator of the expression on the right-hand side of (25) that it becomes a minimum and the whole expression is therefore a maximum when

$$d\sin(\theta+\phi) = \lambda\cos\phi. \tag{26}$$

Equation (26) is equivalent to saying that $1/\Delta$ is then a minimum, as can be seen directly from Fig. 2. The values of $\sin^2\vartheta/\sin^2\epsilon$ have been plotted in Fig. 3, as functions of the angle 2ϵ for six settings of the crystal indicated by the

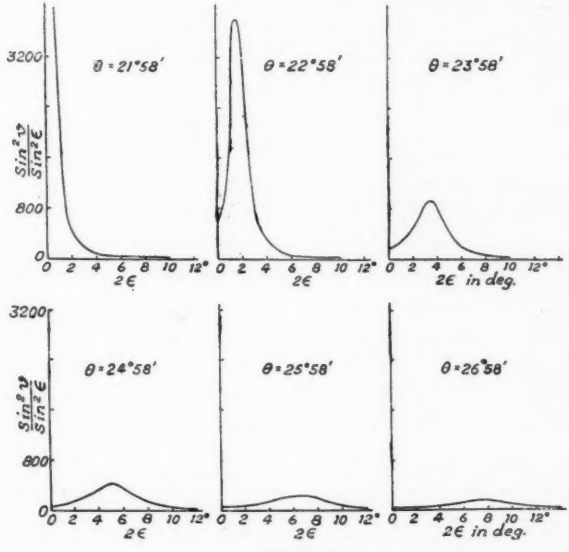

FIG. 3

Graph of the Function $\sin^2\vartheta/\sin^2\epsilon$

different glancing angles of incidence θ entered in the figures. The particular case chosen is one in which $\theta_c = 21° 58'$; in the first of the six settings, θ has the value θ_c, and in the others increases by successive steps of one degree.

It will be seen that the peak of intensity which appears in the first setting coinciding with the classical reflection rapidly falls off and is replaced by a relatively weak hump in the curve which spreads over many degrees of arc. The actual value of the numerical factor $\sin^2\vartheta/\sin^2\epsilon$ also falls off rapidly and becomes insignificant as the crystal is turned away from the correct setting for a classical reflection.

We have in the foregoing analysis tacitly made certain simplifying assumptions, *viz.*, that there is only one kind of elastic waves to be considered, that the velocity of the waves is a constant and that the atomic displacements due to the waves are in every case normal to the crystal planes. In reality, there are three sets of elastic waves possible, their velocity is a function of the direction of travel of the waves, and the directions of the displacement are different for the three sets of waves. It should be remembered, however, that the three sets of waves would not all be equally effective in varying the structure amplitudes of the lattice planes. A movement of the atoms parallel to the lattice planes would have no X-ray effect and we may therefore exclude from consideration the types of waves which give rise to such displacements. Further, only such waves as have their wave-fronts roughly transverse to the lattice planes would produce a scattering of X-rays in directions which are appreciably displaced from the static reflections, and are therefore within the range of observation. It follows that we are principally concerned with distortional waves travelling in directions nearly parallel to the lattice planes under consideration and giving atomic displacements nearly normal to them. Hence, the simplified treatment we have adopted should be a fair approximation to the truth. The variation of the velocity of the elastic waves with the direction of travel may be readily taken account of in our formulæ. In any event, such corrections as may be necessary would not affect the broad result which emerges from the theory, namely that the elastic waves produce only a diffuse scattering of the X-rays with very low intensity and not a geometric reflection of the X-rays in any particular direction.

It may be emphasized that the humps of intensity in the X-ray scattering curves appearing in Fig. 3 correspond to the elastic waves of greatest wavelength or lowest frequency operative in such scattering. Indeed, the smaller the angle at which the hump or maximum appears, and the more pronounced it therefore is, the lower would be the frequency of the elastic waves responsible for it. Accordingly, it is sufficient, as we have done, to take the energy of the individual vibrations as KT and to treat the problem classically. *At low temperatures, therefore, these maxima of scattering intensity should*

weaken still further and become altogether negligible. This should be so even for crystals of high elasticity, such as diamond, so long as we are considering the X-ray effects due to the elastic vibrations of lowest frequency for which $h\nu^* < KT$.

7. *Quantum Reflection by Infra-Red Vibrations*

The geometric law of dynamic reflection (10) indicates that when the X-rays are incident on the lattice planes at an appropriate angle, the static and dynamic reflections appear simultaneously and in the same direction. The length of the phase waves Δ of the lattice vibration is then infinite, in other words, the atomic vibrations have everywhere the same phase. To enable us to evaluate the dynamic structure factor, we require to know the geometry of the particular mode of vibration as well as its actual amplitude. The former may be derived from a knowledge of the crystal structure and atomic forces, while the latter is determined by the energy of the vibration. The entire crystal being regarded as a single dynamic unit, the energy associated with a single non-degenerate mode of its vibration would be KT on the basis of classical mechanics or $h\nu^*$ according to quantum mechanics. In considering the infra-red or monochromatic vibrations, however, the crystal must be considered as a system having a great number of identical or nearly identical frequencies. To obtain an idea of the results to be expected in consequence of this fact, we may make the simplifying assumption that all the N frequencies of the system are identical, N being the number of lattice cells in the crystal. It follows that the amplitude of the N modes of vibration should be superposed. Each *cell* in the lattice would then have energy KT (classical mechanics) or $h\nu^*$ (quantum mechanics). The resulting amplitudes of vibrations would be considerable and the dynamic structure factor would no longer be negligibly small in comparison with the static structure factor. Considering also the identity of the phase of the vibration in the N cells, it follows that it would result in a dynamic X-ray reflection having an intensity proportional to N^2 and comparable with the intensity of the usual static reflections. In the language of quantum mechanics, we may express this by saying that the crystal takes up an energy of vibration $h\nu^*$ from the X-ray photon $h\nu$ which is reflected by the lattice planes with diminished energy $h(\nu - \nu^*)$, but that the probability of such a process occurring is increased N-fold by the fact that all the N cells co-operate, their frequencies, amplitudes and phases of vibration being identical.

On the basis of these ideas, we may evaluate the structure factor for a dynamic reflection when it appears in the same direction as a possible static reflection. Denoting by m_p the mass of the pth atom in the unit cell

and by ξ_p its displacement from the position of equilibrium, the energy of a vibration of frequency ν^* may be written as

$$\sum_p 2\, m_p\, \xi_p^2\, \pi^2 \nu^{*2} = h\nu^*. \tag{27}$$

From this we have

$$\sum_p \tfrac{1}{2}\, m_p\, \xi_p^2 = \frac{h}{4\pi^2 \nu^*}. \tag{28}$$

If the geometry of the vibration is known, we may evaluate the ξ_p's from (28). Resolving each ξ_p in a direction normal to the chosen crystal planes, we obtain its component α_p and thence also ζ_p which appears in the dynamic structure factor. The latter may thus be determined for any particular mode of vibration and for the particular set of crystal planes. A similar procedure would have to be followed if we wish to consider any other possible mode of infra-red vibration or any other set of lattice planes. Taking $h = 6{\cdot}55 \times 10^{-27}$ erg. sec. and with $m_p = 40 \times 10^{-24}$ gm. and $\nu^* = 6 \times 10^{12}$ sec.$^{-1}$ as representative values, the quantity $\sqrt{h/4\pi^2 m_p \nu^*}$ comes out as a length of the order 0·1 A.U. The ratio of $J_1(\zeta_p)$ and $J_0(\zeta_p)$ appearing respectively in the expressions for the dynamic and static factor is then of the order 1 : 20 for an average crystal. *In other words, under the most favourable conditions, the quantum or modified reflections have intensities which are of the same order of magnitude as the classical or unmodified reflections though, as a rule, definitely weaker.*

It is worthy of remark that if a crystal has several possible infra-red modes of vibration, those of the lowest frequencies would in general, as indicated by (28), produce the most important X-ray effects. The special importance of the modes of lower frequency would however be less marked on the quantum theory than on the classical mechanics; this becomes evident on writing KT instead of $h\nu^*$ on the right-hand side of (27). We would then have ν^{*2} instead of ν^* in the denominator of (28). The question as to which of the possible infra-red modes is most effective is, however, not so summarily to be disposed of. Actually, each set of crystal planes would have to be considered separately in relation to the various possible modes of vibration in the lattice. It may well happen that the dynamic structure amplitude of a particular set of crystal planes is largely derived from one of the possible modes of vibration, while another set of planes is chiefly influenced by some other mode. It may also well happen that the dynamic structure factors determined by the aggregate effect of all the possible modes of vibration are widely different for different sets of crystal planes and bear no simple relation to the static structure factors of the same

planes. Such special features would be characteristic of the individual crystal structure and of the particular modes of its infra-red vibration.

The simplifying assumption made above that all the N modes of vibration of the lattice have an identical frequency is equivalent to stating that the only possible phase wave-length is the largest possible, *viz.*, $\Delta = \infty$. This is evidently an extreme assumption, and it would be more reasonable to expect that while the great majority of the possible modes of vibration correspond to a very great phase wave-length, the remainder correspond to lesser values of Δ, thus enabling the dynamic reflections to appear at other settings of the crystal as indicated by equation (10). It would then follow that the intensity of the dynamic reflections should diminish rapidly as the crystal is moved away from the setting at which the static and dynamic reflections appear superposed. The fall in intensity would, in fact, represent the distribution of the possible modes of vibration in respect of phase wave-length.

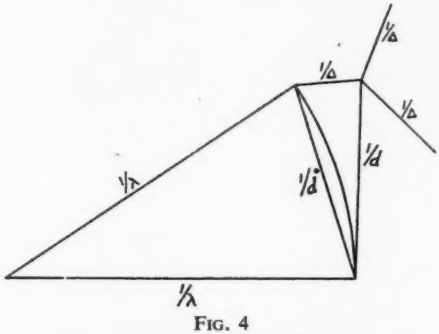

FIG. 4
Geometry of Quantum Reflection

The situation indicated above is indicated graphically in Fig. 4. The reciprocal of the phase wave-length, namely $1/\Delta$, which we may denote by δ is represented as a vector drawn from the terminus of the vector $1/d$ which gives the spacing and setting of the crystal planes. The great majority of the possible values of δ congregate at the origin $\delta = 0$. There are, however, some which spread out along the lines representing the permitted directions of the phase-wave normal. The quantum reflections would then appear at the point or points on the sphere of reflection at which the vectors δ thus drawn meet the latter. As already explained, the dynamic reflections need not necessarily lie in the plane of incidence. The restriction of the vector δ to fall in specific directions differentiates our present case (Fig. 4) from that of quantum scattering also represented geometrically

in Fig. 2. Such a restriction arises naturally from the fact that we are now concerned, *not* with a displacement of the lattice cell as a whole in some *arbitrary direction*, but with a *specific* mode of vibration of the atomic grouping within the cell. The symmetry of such atomic grouping, the nature and magnitude of the inter-atomic forces and especially the geometrical characters of the particular mode of vibration necessarily determine the possible orientations of the phase-vector δ. In the ideal case, therefore, we may expect this to lie in one or another of certain *precisely* defined directions related to the symmetry of the crystal and the symmetry of the mode of vibration. The quantum reflection would then appear, as indicated in Fig. 4, in a *sharply defined* direction (or in sharply defined directions, if, for instance, considerations of symmetry require that there should be several possible directions of the vector δ). It is evident that such a restriction of the phase-vector δ to specific directions would result in a very great increase in the intensity of the observable effects; in fact, the sharper the reflection, the more intense it would be and therefore the more easily observed. Thus, even if only a small fraction of the total number N of possible modes of vibration appear as stragglers from the point $\delta = 0$, their restriction to specific directions of δ should enormously increase the visibility of their effects.

We cannot however always expect the dynamic reflections to exhibit the same sharpness and precisely defined geometric character as the static reflections by the crystal planes. When, for instance, the effects of different possible modes of vibration are superposed, or when the binding forces in the crystal are relatively weak and are further disturbed by thermal agitation, a certain lack of precision in the direction of the phase-vectors would be inevitable. In such a case, the quantum reflections would necessarily be a little diffuse. Since, however, the majority of values of the vector δ congregate at the point $\delta = 0$, all the possible directions of the vector must necessarily crowd together as we approach the common origin. Hence, the reflections should appear not only more intense but also more sharply defined as the crystal setting approaches the position in which the static and dynamic reflections coincide. The same considerations indicate that at the lowest possible temperatures when the disturbing influence of thermal agitation is removed, the diffuseness, if any, of the quantum reflections arising from its presence should diminish and disappear.

As indicated in earlier discussions, the distribution of the N possible modes of vibration amongst various values of the phase-wave vector δ, is closely connected with the perfection of the monochromatism of the vibration

frequency. The distribution should, in fact, run parallel to the distribution of the N modes amongst the various possible frequencies of vibration. The fine structure of the spectral lines in the infra-red region should thus stand in the closest relation to the variation in intensity of the quantum X-ray reflections with the crystal setting. It is known from studies on light scattering that the spectral lines representing the lattice vibrations, especially those of the lowest frequencies, become sharper at low temperatures. This effect is presumably due to the removal of the thermal agitation which disturbs the precisely defined geometric character of the infra-red vibrations and therefore also their monochromatism. Observations at low temperature should thus indicate a closer approach of the X-ray effects towards the ideal behaviour, *viz.*, the appearance of sharply defined and correspondingly more intense dynamic reflections. Whether temperature directly affects the distribution of the N possible modes in the δ diagram, in other words tends to transfer a larger proportion of the modes to the origin $\delta = 0$, thereby diminishing the number of stragglers must, for the present remain, an open question. It can only be answered when we are in a position quantitatively to formulate the distribution law. The strength of the inter-atomic bindings within the lattice cell, and the strength of the forces which link the lattice cells to each other and make the whole crystal a coherent solid must necessarily enter into such a distribution law. Only in the ideal case when the lattice cells are firmly linked with each other and the influence of thermal agitation is negligible would be the assumption that the atoms within the lattice cells all vibrate together with identical frequency, amplitude, and phase approach towards the complete truth. It follows that our calculation of the intensity of the quantum reflection from equations (27) and (28) should be regarded as setting an upper limit to the intensity of such reflections which would be approached only in the most favourable cases.

8. *Temperature Factor for Quantum Reflections*

The quantum theory of radiation is an application of quantum mechanics to a consideration of the interrelations between matter and radiation. In our present problem we are concerned with the effect of passage of a train of waves through a regularly stratified medium in the particular case when the stratifications may, in part, be time-periodic. If the existence of such time-periodic stratifications be assumed, classical optics indicates—quite independently of all atomistic or quantum theoretical considerations—that both static and dynamic reflections would be observable under appropriate conditions, the latter appearing with a change of frequency. We translate this result into the language of the quantum theory by saying that the

change of frequency arises from the exchange of energy between the photon and the medium, while the optical condition for a dynamic reflection is equivalent to the conservation of momentum in their encounter (Tamm, 1930). Quantum theory indicates that there is a finite probability of a vibration quantum being created or destroyed in the encounter if there be a finite interaction energy between the radiation field and the vibrations of the solid. The fundamentally new feature arising in the quantum mechanics not indicated by the classical or semi-classical theories is that the vibrations, even if non-existent in the absence of the radiation, would be created by it. This is the basis of our equation (27) in which the energy of the oscillation is put equal to $h\nu^*$ and which correctly represents the situation at the lowest temperatures. In the presence of thermal agitation, we have to merely add a contribution due to its effect. In other words, instead of $h\nu^*$ we write the energy of the vibration in equation (27) as

$$h\nu^*\left(1+\frac{1}{e^{h\nu^*/KT}-1}\right). \tag{29}$$

The second term within the brackets is the Planck factor. The justification for its inclusion is that the probability of the creation of a vibration quantum would be proportional to the number of such quanta present, and (29) is therefore only valid when we are considering encounters in which the number of vibration quanta is *increased* by the incidence of radiation. In considering the cases in which the number is *diminished*, we must evidently take the energy as

$$h\nu^* \cdot \frac{1}{e^{h\nu^*/KT}-1}. \tag{30}$$

In our present problem, the effects of both types of encounters appear superposed, and we may therefore take the energy as the sum of (29) and (30), *viz.*,

$$h\nu^* \cdot \frac{e^{h\nu^*/KT}+1}{e^{h\nu^*/KT}-1}. \tag{31}$$

The effect of thermal agitation would be thus to increase the intensity of the quantum reflection or the quantum scattering as the case may be, by the factor

$$\frac{e^{h\nu^*/KT}+1}{e^{h\nu^*/KT}-1}, \tag{32}$$

which we shall refer to as the temperature factor in what follows.

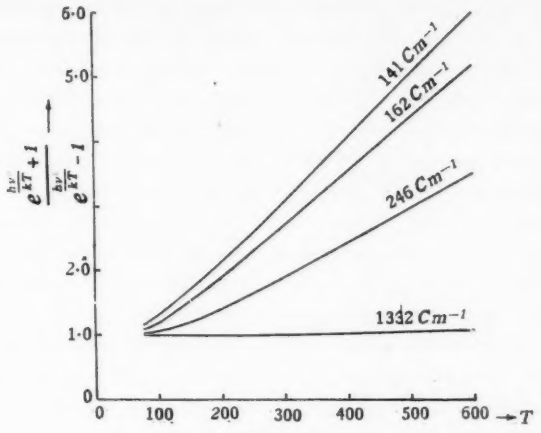

FIG. 5

Temperature Factor of Quantum Reflection

In the particular cases when $h\nu^* \gg KT$, *viz.*, when the frequency of vibration is very high or the temperature is very low, the temperature factor reduces to unity and (31) becomes simply $h\nu^*$. On the other hand, when $h\nu^* \ll KT$, *viz.*, when the frequency of vibration is very low or the temperature is very high, the expression (31) reduces to 2 KT. The numerical factor 2 indicates that we are now dealing with the sum of the two effects having the frequencies $(\nu \pm \nu^*)$, whereas previously we are only concerned with $(\nu - \nu^*)$. Thus, at sufficiently high temperatures, the intensities of dynamic reflection and scattering become proportional to the absolute temperature. At what stage this occurs depends on the value of ν^*. To illustrate this feature, the value of the temperature factor has been drawn as a function of the absolute temperature in Fig. 5 for a number of different values of ν^*. These are indicated in each case in spectroscopic units against the curves. It will be seen that all the curves tend asymptotically to the value unity at low temperatures. For low values of ν^*, the curve begins to rise steeply at a fairly low temperature, while for high values of ν^*, it remains nearly horizontal over a large range of temperature.

The foregoing is, of course, a simplified treatment, but it is sufficient to indicate the main features of the case. The treatment assumes that the intensity of dynamic reflection is proportional to the energy of the vibration giving rise to it. Such proportionality does not necessarily hold good when the thermal agitation is too violent. It should also be remarked that we are considering the different possible modes of infra-red vibrations as independent

of each other, in other words, we are neglecting their mutual influence. Even when such neglect of the interactions is justified, we must necessarily consider their effects as superposed on each other. When there are several infra-red modes of widely different frequencies, it is possible that the temperature factor may be effectively different for the different sets of lattice planes in the crystal. In other words, those lattice planes whose structure amplitude is noticeably affected by the infra-red vibrations of lowest frequency would show a large temperature factor, while those which are sensibly influenced only by the modes of higher frequency would show a relatively small temperature variation. That such a situation would arise in crystals which are highly anisotropic in structure is extremely probable. That it may occur even in isotropic crystals becomes evident when we recall that the atomic density and the structure amplitude vary enormously for the different planes of a crystal. Some of the planes in a crystal have special properties, *e.g.*, cleavage, determined by the grouping of the atoms and the nature of the atomic bindings. These factors also determine the modes of atomic vibration possible. Hence, it should not be a matter for surprise to find that the temperature factor for dynamic reflection varies greatly for different planes also in isotropic crystals.

9. *Temperature Factor for Classical Reflections*

We have already noticed in Section 5 that the presence of a vibration which endows the lattice units with a dynamic structure factor simultaneously results in a reduction of the static factor. The reduction arises from the term $J_0(\zeta_p)$ which multiplies the atomic structure factor, this being the same for all the p atoms in the unit cell in the case of an elastic vibration, but different for the p different atoms in the case of an infra-red vibration. The energy of an *individual* vibration being only $h\nu^*$ multiplied by the relevant factors, see (29) and (30), the diminution of the static structure factor produced by it is negligible. The infra-red vibrations, however, have an N-fold degeneracy. The vibration of the atoms resulting from the superposition of the N modes would therefore be sensible and therefore also the diminution of the static structure factor produced by it. When the static reflection appears, the dynamic reflection is also superposed on it and is therefore effectively an addition to its intensity. Nevertheless, if the intensities of the two types of reflection are assumed to be proportional to the squares of their respective structure factors, the diminution of intensity is not compensated by such superposition. In other words, *the possibility of a quantum X-ray reflection by the crystal planes necessarily diminishes the intensity of the classical X-ray reflections by the same planes.*

In practice, there may be several modes of infra-red vibration possible. Their effect and also the *aggregate* effect of the low-frequency elastic vibrations of the lattice on the static structure factor of the atoms requires consideration. We therefore proceed to examine the case in which several different modes of vibrations are superposed. We write for the displacement of the pth atom

$$D_p = d_p + \sum_n a_{pn} \cos (2\pi \nu_n^* t + z_{pn}). \tag{33}$$

The secondary radiations from the atom have then as their periodic part

$$\cos [2\pi \nu t - Z_p - \sum_n \zeta_{pn} \cos (2\pi \nu_n^* t + z_{pn})]. \tag{34}$$

The expansion of this in a series of Bessel functions is most easily carried out by writing (34) in an exponential form. It then appears as a product of a series of terms containing ν, ν_1^*, ν_2^*, etc., in the exponentials. On writing out the products after expansion in a series of Bessel functions, we get terms which are periodic in ν, $(\nu \pm \nu_1^*)$, $(\nu \pm \nu_2^*)$, etc., and also periodic terms involving overtones and combinations of ν_1^*, ν_2^*, etc. Neglecting these latter, the multiplier of the atomic structure factor for the frequency ν comes out as

$$\prod_n J_0 (\zeta_{pn}) \tag{35}$$

while the multiplier for the atomic structure factor for the frequency $(\nu \pm \nu_m^*)$ is

$$J_1 (\zeta_{pm}) \cdot \prod_{n \neq m} J_0 (\zeta_{pn}). \tag{36}$$

For values of ζ which are not too large, we may use the approximation

$$J_0 (\zeta) = e^{-\frac{1}{4}\zeta^2} \text{ and } J_1 (\zeta) = \tfrac{1}{2} \zeta. \tag{37}$$

Thus, the multiplier for the static structure factor of the atom is

$$e^{-\sum_n \frac{1}{4} \zeta^2_{pn}} \tag{38}$$

the summation in the exponent being over all the n different frequencies of vibration. The multiplier for the dynamic structure factor of the atom for the frequency $(\nu \pm \nu_m^*)$ is

$$\tfrac{1}{2} \zeta_{pm} \cdot e^{-\sum_{n \neq m} \frac{1}{4} \zeta^2_{pn}} \tag{39}$$

the summation in the exponent being now made over all the frequencies of vibration except ν_m^*. It appears from (38) that all the modes of vibration assist in diminishing the static atomic structure factor, while (39) indicates that the dynamic structure factor for a particular frequency of vibration is

diminished in the same way by all the other modes of vibration. The ratio of (39) to (38) is

$$\tfrac{1}{2}\,\zeta_{pm}:\ e^{-\frac{1}{4}\zeta_{pm}^2} \tag{40}$$

and depends only on the displacements of the atom due to the vibration of frequency ν_m^*. In this particular sense, each different vibration may be regarded as acting independently of all others, in other words as giving a quantum reflection of which the intensity in relation to the classical reflection is determined exclusively by its own amplitude.

In the summation indicated by the exponent in (38), we have to include all the frequencies of vibration of the lattice. We recall that

$$\zeta_{pn}=\frac{4\,\pi a_{pn}\,\sin\,\theta}{\lambda}, \tag{41}$$

where a_{pn} is the displacement of the pth atom resolved normal to the crystal plane due to the vibration of frequency ν_n^*, the actual displacement ξ_{pn} being given by the geometry of the vibration and its energy. Considering the elastic vibrations first, we have already noticed that those of the lowest frequencies give the largest atomic displacements. On the other hand, the modes of the higher frequencies are far more numerous. Thus, the entire range of possible frequencies of elastic vibration would contribute towards determining the product (38) which alters the atomic structure factor. The treatment of the problem by Debye, Waller and Laue however greatly exaggerates the part which the elastic vibrations of the lattice play in this respect. Firstly, there is no justification for assigning all the 3 Np degrees of freedom to the elastic vibrations. The maximum number which can properly be so assigned is 3 N, the remaining $(3p-3)$ N degrees of freedom representing the infra-red or monochromatic vibrations of the lattice. Then again, the actual frequency limit for the elastic spectrum is automatically reduced by the diminution in the number of degrees of freedom allotted to it. Thirdly, the semi-classical way in which the quantum theory of specific heats and the zero point energy are usually brought into the X-ray problem is, of course, invalid. Finally, in the vast majority of actual crystals, the Einstein or monochromatic vibrations, besides being more numerous, have often quite low frequencies and therefore make a notable contribution to the thermal energy. Their influence on the intensity of the classical reflections indicated by (38) should therefore be of great importance, in fact much more so than that of the elastic vibrations of the lattice.

It follows from what has been stated above that there should be a considerable degree of correlation between the intensity of the quantum

reflection by a particular set of crystal planes and the temperature variation of the intensity of the classical reflection by the same set of planes. An intense quantum reflection can only arise if the structure amplitudes are strongly influenced by the possible modes of infra-red vibration with a corresponding diminution of the static structure factor. We should then ordinarily expect a notable temperature effect of the intensity of classical reflection, *pari passu* with an increase of the intensity of quantum reflection with rising temperature. Since however, the static and dynamic structure factors for the unit cell are determined by different considerations, the correlation indicated above is not necessarily to be observed in all cases.

10. Summary

The ideas indicated in the preceding paper are here worked out quantitatively. The secondary radiation from an oscillating atom in a crystal traversed by X-rays is analysed into its frequency components. It is shown that the interferences to which each component of altered frequency gives rise are determined jointly by the positions of the atoms and the phases of their vibration. It follows that besides the static reflections of unmodified frequency by the crystal planes, we would also have dynamic reflections of altered frequency. The geometric law of such dynamic reflection is derived. The static and dynamic structure factors are deduced and it is pointed out that the elastic and infra-red vibrations of the lattice stand on a different footing in respect of these factors. Considering first the elastic vibrations, formulæ are obtained and graphs are drawn which show that such vibrations give rise to a diffuse scattering of the X-rays with low intensity proportional to the number of lattice cells. The N-fold degeneracy of the monochromatic infra-red vibrations, on the other hand, results in their giving true geometric reflections with altered frequency and with intensity proportional to the square of the number of lattice cells. The intensity of such reflection is evaluated on the basis of the quantum theory of radiation. The variation of the intensity, direction and sharpness of the quantum reflections with crystal setting is discussed. A formula is then obtained for the temperature variation of the intensity of the quantum reflections. The temperature factor for the intensity of the classical reflection is also written down and the extents to which the elastic and infra-red vibrations respectively contribute to it are discussed.

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QUANTUM THEORY OF X-RAY REFLECTION: EXPERIMENTAL CONFIRMATION

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1. Introduction

The fundamental discovery that the lattice planes in a crystal give rise to monochromatic X-ray reflections of a second kind involving a change of frequency was made in the laboratories of this Institute and announced at the Easter meeting of the scientific societies of Bangalore held on the 22nd March 1940. It was an essential part of the discovery that the experimental characters of the phenomenon as actually observed were such as to place it entirely outside the range of the accepted theories in X-ray optics. The explanation of the newly discovered phenomena, in fact, demanded the introduction of radically new ideas regarding the nature of the vibrations possible in crystal lattices and also regarding the nature of the interactions which occur when X-rays traverse a crystal. These new ideas were indicated simultaneously with the new experimental facts in an article in *Current Science* for April 1940. Though new to X-ray physics, the ideas set out in that article had already emerged more or less clearly from the spectroscopic investigations on the scattering of light in crystals which had previously been engaging the attention of the laboratory.* The application of these ideas in the field of

* A brief summary of these investigations and the ideas emerging therefrom will be found in the Franklin Medal Day lecture to be published in the *Franklin Institute Journal* for September 1941.

X-ray research was thus almost inevitable. The further investigations which have since been continued systematically at this Institute have not merely confirmed the statements made in the first publication, but have also shown that the new X-ray results taken together with the earlier spectroscopic studies compel revolutionary changes in our concepts of the solid state. In fact, the X-rays directly demonstrate what had been previously only inferred from the optical evidence, namely, that the lattice vibrations appearing as monochromatic lines in the spectrum of a crystal possess a degree of orderliness and coherence which is astonishing and truly as remarkable as the orderliness of the static arrangement of the atoms characteristic of a crystal. The optical and X-ray methods of investigating the lattice vibrations in crystals thus stand in the closest relation, supplementing each other. The optical methods enable us to analyse the infra-red vibrations into their frequency spectrum and only indirectly to infer their geometric character. The X-rays, on the other hand, enable us directly to ascertain the geometrical characters of the vibration and only indirectly to infer the frequency changes involved.

The clear-cut enunciation of the new facts and ideas put forward in April 1940 was made possible largely by the deliberate choice of diamond as the crystal round which the investigations have principally centred. The known perfection of this crystal, the simplicity of its structure, the possibility of using relatively soft X-rays in working with it, and above all, the geometric precision with which it exhibits the new phenomena have enabled the latter to be understood much more clearly than would have been otherwise possible. For this reason, the present article will be devoted wholly to the results of the experimental studies made with diamond. It will be shown, on the one hand, how the experimental facts totally exclude any explanation of the type based on the original theories of Debye, Waller and Faxén, with or without such further modifications as have been recently suggested. It will, on the other hand, be shown how completely the experimental facts fit into the scheme of new ideas expounded and developed quantitatively in the two preceding papers. It must not be imagined however that the case for the new theory rests exclusively on the facts observed with diamond. So far from this being the case, it may be said that a careful and unprejudiced examination of the facts with any crystal is sufficient to show that the efforts recently made by several workers, notably Zachariasen, Max Born and the group at the Royal Institution to base an explanation of the new X-ray facts observed at this Institute on the basis of the existing theories or modifications thereof are not on the right lines. In the earlier paper on basic ideas, the effects indicated by the theories of the Debye type are set out and contrasted with those indicated by the quantum theory of X-ray reflection, and a series of experimental

criteria are put forward enabling a discrimination between the two. In the papers which follow in these *Proceedings*, these criteria have been applied in several cases, and in every case the verdict of the facts has been in favour of the new ideas. Equally striking has been the success of the new ideas in dealing with problems of the solid state which have hitherto proved baffling, *e.g.*, the large deviations of the observed specific heats of elementary solids, such as metals, from those indicated by the Debye specific heat formula. Far from such a failure of the Debye theory being surprising, it is a necessary consequence of the idea that the lattice spectrum of every crystal includes Einstein or monochromatic frequencies of vibration. Mr. Bisheswar Dayal has shown in a series of papers which will appear in the next issue of these *Proceedings* that the specific heat curves for metals and other elementary solids find a very simple and complete examination on the basis of these new concepts in crystal dynamics.

2. *Structure and Lattice Spectrum of Diamond*

The specific heat of diamond has been accurately measured by Pitzer (1938) over the range of temperature from 70° T. to 288° T. His data do not fit into the Debye formula, showing deviations as large as fifteen per cent. within this range, if the limiting frequency in the formula is chosen to fit the data at the lower limit of temperature. The cause of this failure becomes apparent when we consider the real nature of the lattice spectrum. The Debye theory of specific heats rests on the belief that the infra-red vibrations of the lattice are physically of the same nature as the vibrations of the acoustic type and form a continuous spectrum of frequencies. That the same idea forms the basis of the crystal dynamics of Max Born and his school is evident from the postulate of the "cyclic lattice" on which the work of that school rests and which has been discussed earlier in these *Proceedings* and shown to be untenable. The Born postulate places the elastic and infra-red vibrations mathematically on the same footing. Its implications become clear when we examine the results of the calculations worked out on its basis by Blackmann, Kellerman and others of that school. The calculations lead to representations of the vibration spectrum which while differing in detail from that assumed in the Debye theory, have nevertheless the same fundamental feature, namely that the vibrations of the extended solid forms a continuous spectrum of frequencies. The lattice spectra of actual crystals as revealed to us by spectroscopic investigations, especially those made at low temperatures, present us with a totally different picture. Indeed, it may be said that the assumptions made in the Debye theory and in the Born crystal dynamics bear no resemblance whatever to the actual facts at such temperatures.

Several different lines of investigation agree in showing that, except possibly in the region of the lowest frequencies where the experimental techniques have not at present been good enough to give a definite answer, the lattice spectrum of diamond consists of sharply defined or monochromatic frequencies. Bhagavantam (1930) investigated the scattering of light in diamond and found numerous sharp lines in the spectrum giving the following frequency shifts in wave numbers per centimetre: 1585, 1480, 1431, 1382, **1332**, 1288 and **1158**. Amongst these, the 1332 line is at least a hundred times more intense than the next most intense line 1158, while the others were just detectable in the spectrum of a large clear white diamond. The 1332 line, besides being intense, is also extraordinarily sharp, in fact exactly as sharp as the exciting radiations. It remains sharp (though with gradually diminishing frequency shift) over the whole range of temperature from 93° T. to 1130° T. Further evidence on the lattice spectrum of diamond has been furnished by the recent investigations of Nayar at this Institute on its luminescence and ultra-violet absorption spectra at low temperatures. As was first noticed by Ramaswamy, diamond exhibits a fluorescent band at 4157 A.U., the same band also appearing in absorption. On cooling down the crystal to liquid-air temperatures, this band shifts to 4152 A.U., at the same time becoming much sharper. Subsidiary bands are also noticed at lower frequencies in fluorescence and at higher frequencies in absorption, the frequency differences between these and the 4152 band being the same but of opposite sign in fluorescence and in absorption. These frequency differences therefore represent the lattice spectrum of diamond. The band at 4152 A.U. is not as sharp at liquid-air temperature as could be desired, and it is greatly to be hoped that this work will be repeated at liquid hydrogen temperatures in some cryogenic laboratory. Nevertheless even at liquid-air temperatures and using the fairly high dispersion provided by an E_1 Hilger spectrograph, Nayar has found that the fluorescence and absorption bands appear resolved into numerous *discrete frequencies*. These are (within about ten wave numbers) 1341, 1252, 1148, 1090, 1010, 960, 784, 681 and 532. There are indications of larger frequency shifts in the same region as those observed by Bhagavantam, as also of several discrete frequency shifts smaller than 532 appearing very feebly in the spectra. Plate XVI, Figs. 4 (*a*), (*b*) and (*c*) reproduce the lattice spectrum of diamond as observed respectively in light-scattering, in fluorescence and in absorption, and exhibit these frequency shifts.

The dynamical theory of the diamond lattice has not at present been worked out with sufficient thoroughness to enable us to explain all these

experimental results. It is noticed, however, that the most intense fluorescence and absorption frequencies fall roughly into two groups. The head of one of these groups is close to the 1332 frequency which appears as an extremely intense and sharp line in light scattering. The nature of the 1332 vibration has been very fully discussed by Nagendra Nath (1934) and was indicated by him as an oscillation relative to each other of the two Bravais lattices of carbon atoms which constitute diamond. Since each carbon atom belonging to one lattice is bound by valence bonds to four carbon atoms in the other lattice, and *vice versa*, such an oscillation would necessarily have a high frequency. Indeed, a calculation based on the known force constants gives a frequency in fair agreement with the observed 1332. The symmetry characters of such an oscillation (Venkatarayudu, 1938) also indicate that it should be active in light-scattering. The identification of the 1332 frequency as that of an oscillation of the two interpenetrating lattices of carbon atoms relative to each other is thus firmly established. The second group of frequencies of which the head is at 784 is completely inactive in light scattering. It is therefore very probable that the oscillations of this group involve movements of the atoms in each Bravais lattice against themselves, alterations of the tetrahedral valence angles rather than the extensions or compressions of the valence bonds determining the observed frequencies.

Examining the structure of diamond, we find that the carbon atoms belonging to the two Bravais lattices appear in the planes parallel to the octahedral faces in separate layers which are alternately at *unequal distances*. It follows from this fact and the considerations set out in the preceding paper that the (111) planes would have their structure amplitudes strongly varied by the 1332 oscillation. A similar situation would also arise in respect of any oscillation in which the movements of some of the atoms in one Bravais lattice are balanced by opposite movements of an equal number of atoms in the other lattice. If, on the other hand, we consider a type of vibration in which the movements of the atoms in one lattice are balanced by opposite movements of the remainder of the atoms in the same lattice, it is easily seen that the structure amplitudes of the octahedral planes would remain unaffected. It is thus evident that only the **1332** vibrations or other vibrations of similar character would influence the structure amplitudes of these planes. A simple calculation on the basis of the theory set out in the preceding paper shows that in spite of the high frequency involved in such oscillations, dynamic reflections of notable intensity should be given by the (111) planes. On account of the high frequency of the associated vibrations of the lattice, such reflections should be practically insensitive to variations of temperature.

The crystal spacings in diamond giving the classical X-ray reflections are of two kinds. In one set which includes the spacings parallel to the octahedral faces, the alternate layers of carbon atoms appear unequally spaced in the ratio of 1 : 3. In the second set, which includes the planes parallel to the forms of the cube and the dodecahedron, the planes appear equally spaced. In the planes parallel to the dodecahedral faces, the carbon atoms belonging to the two Bravais lattices appear interspersed with each other in equal numbers. It follows that these planes are incapable of giving a dynamic reflection as a result of the relative oscillation of these two lattices. This conclusion, however, only refers to this particular mode of vibration having the high frequency of 1332 wave-members. There are numerous other modes of vibration of the lattice with discrete frequencies, some of which are as low as 127, 178, 303 and 421 wave-numbers (Nayar, 1941). In such vibrations, there can be no doubt that the atoms in each Bravais lattice oscillate against each other, that is, some of the atoms move one way and the others move the opposite way to balance the oscillation. The extreme feebleness with which the frequencies lower than 532 appear in fluorescence and absorption probably indicates that such vibrations have a relatively small *a priori* probability. Nevertheless, a low frequency involves a correspondingly larger amplitude of vibration. Hence, the planes in the crystal which cannot give a dynamic reflection associated with the 1332 vibration may nevertheless give observable reflections associated with some of the vibrations of the lattice with lower frequencies. Such reflections would be indicated by their intensity being more temperature-sensitive than the reflections associated with the high-frequency vibrations.

3. *Specular Character of Quantum Reflections*

Amongst the many items of supporting experimental evidence set out in the publications by the present writers (1940) announcing the discovery of quantum or modified reflection, one of the most cogent which was duly emphasized was the truly geometric or specular character of the reflections associated with the (111) planes of diamond. This feature by itself and apart from all other evidence was sufficient proof that the phenomena described in those papers lay entirely outside the scope of X-ray optics as it existed before the announcement of the discovery. In view of the importance of this feature and especially of the fact that it is absolutely fatal to the attempts made by Max Born and others to interpret the phenomena on the basis of the Debye-Born crystal dynamics, we shall here consider it in some detail.

Even in the photographs published with our earliest communications (*Current Science*, April 1940 and *Nature*, 27th April 1940), it was evident

that the quantum or dynamic reflections given by the (111) planes of diamond were just as sharp as the ordinary Laue reflections by the same planes. While the Laue reflections appeared as elliptic spots, the quantum reflections were round in shape and had about the same diameter as the major axis of the Laue spots. These features are readily understood when the angular divergence of the incident beam is considered and it is borne in mind that a quantum reflection can occur at any incidence of the X-rays on the crystal planes. A detailed discussion of the geometric aspects of the quantum X-ray reflections in diamond by Mr. P. R. Pisharoty has already appeared in a recent issue of these *Proceedings* (1941). Mr. Pisharoty has proved that the appearance of the quantum reflections as observed in the photographs for all possible settings of the crystal is just what we should expect if they were perfectly geometric.

In actual experimental work with X-rays, the radiation from the source is necessarily divergent. The extent and manner in which such divergence may be advantageously limited depends both on the aim of the investigation as well as upon the material under study, *viz.*, upon the thickness or area of the crystal. In investigating phenomena of low intensity, an undue restriction of the divergence of the beam would merely increase the difficulties of the investigation without advancing its purposes in any way. Thus, for instance, in the present problem, when we wish to decide whether we are dealing with a sharp reflection or a diffuse scattering, instead of reducing the aperture excessively, it is preferable to retain it at a reasonable value and prolong the photographic exposures as much as possible. In such circumstances, a geometric reflection would not enlarge in area, while a diffuse scattering would progressively widen out. Using the technique here indicated, it is easy to decide the question whether the quantum reflections in diamond enlarge their angular extension when the crystal is moved away from the setting at which the quantum and classical reflections coincide. By not reducing the width of the X-ray beam unduly, it is possible to record the spots with fair intensity even when the crystal setting is altered by as much as 6° in either direction. It will be seen from the photographs reproduced in Plate XVII, Figs. 5 (*a*) to (*k*) that the extension of the quantum reflections remains constant over this whole range of settings, while if it were due to a scattering of the X-rays associated with the reflections of the usual kind, it should enlarge rapidly in area. One has only to glance at the photographs in Fig. 5 and then turn to the set of curves reproduced in Fig. 3 of the preceding paper showing how the distribution of intensity of scattering of X-rays varies with the setting of the crystal to realise the futility of any attempt to explain the actual phenomena in terms of the scattering theory.

The classical and quantum reflections have a different origin and obey different geometric laws. Nevertheless, they are both geometric reflections, and optical principles indicate various simple criteria which can be employed to test their nature as such and which would reveal the correct position immediately if the quantum reflection were not an independent phenomenon. Various factors in the experimental technique are capable of variation, *e.g.*, the area and angular divergence of the incident X-ray beam, as well as the area and the thickness of the crystal irradiated by it. These variations would influence the intensity and the angular spread of the two effects in a very different manner if they were not essentially similar phenomena. Actually, we observe a complete parallelism in the behaviour of the classical and quantum reflections when the experimental factors are varied separately or together. It is well known, for instance, that the spots in a Laue pattern diminish in extension when the X-ray beam is made narrower, and that such diminution in size cannot be prevented from occurring by merely prolonging the photographic exposures. Precisely the same effect is observed with the quantum reflections by the (111) planes in diamond. These are reduced in extension by limiting the area of the X-ray pencil in much the same way and in the same proportion as the ordinary Laue reflections, longer exposures not altering the situation. It is also noticed that the relative intensity of the Laue and quantum reflections remains unaltered by such procedure, thus proving that we are dealing with true geometric reflections in both cases and not a reflection in one case and a scattering in the other.

The classical X-ray reflections by the lattice planes of crystals appear in directions which are geometrically definable with a degree of precision depending on the perfection of the crystal. Diamond, for instance, may be so perfect that the setting at which it reflects monochromatic rays with the maximum intensity is probably definable with as great an accuracy as the wave-length can itself be specified. In the case of the quantum reflection, we are concerned not only with the geometric perfection of the crystal but also with its *spectroscopic* perfection, that is to say, with the monochromatism of the infra-red vibrations of its lattice. As will be seen from Fig. 4 (*a*) in Plate XVI, the monochromatism of the 1332 vibration of the diamond lattice, even at ordinary temperature, is of the most remarkable kind. Accordingly, we should expect that the quantum reflections by the (111) planes which owe their origin to it should have a precisely definable geometric character and should be unaffected in their sharpness by the setting of the crystal. A rigorous test of this question is not so easy as in the case of the classical reflections, for the quantum reflections can occur independently of the angle of incidence of the X-rays on the crystal,

Hence, an angular divergence of the incident beam and therefore also of the reflections can easily be mistaken as indicating a lack of geometric perfection of the latter. The severity of the test which can be made depends on the possibility of obtaining an X-ray beam with small lateral extension and angular divergence but of sufficient intensity to record the quantum reflections in a reasonable time. As the intensity of the reflections falls off with extreme rapidity when the crystal setting is turned away so as to separate the classical and quantum reflections, it is evidently not easy to push the question to the final limit. It may be stated, however, that, *the quantum reflections by the* (111) *planes of diamond are geometrically as perfect as can be experimentally ascertained at the present time*. This is shown by the photographs reproduced by Figs. 6 (*a*) and (*b*) in Plate XVIII. In these photographs, the quantum reflections by the (111) planes have been recorded using a fine rectangular slit 100 millimetres deep and 0·15 millimetre wide, and a cleavage plate of diamond 0·76 millimetre thick. The width of the reflections as measured on the plates is no greater than that to be expected from the finite lateral extension of the beam, its angular divergence and the thickness of the plate used. It is specially noteworthy that the reflection as recorded on the plates shows no detectable widening when the crystal setting is altered so as to make the quantum reflection move away from the Laue reflection in one direction or the other by several degrees.

These facts show that there is no ground for the belief entertained by some X-ray workers in the Debye-Waller-Faxén theory of X-ray scattering as a possible explanation for the phenomena discovered with diamond at this Institute. So striking are the facts that even the advocates of the scattering theory have been compelled to take the illogical step of referring to the phenomena as a "diffuse reflection" instead of as a "diffuse scattering" which would be the correct nomenclature for them to adopt on the basis of that theory. Indeed, the designation of "diffuse reflection" as applied to the case of the (111) quantum reflection of diamond is quite misleading. Actually, these reflections are probably as sharp or sharper than the classical reflections of X-rays by the lattice planes of many crystals of the ordinary or imperfect type.

4. *Geometric Law of Quantum Reflection*

Any discussion regarding the geometric law of the quantum reflection presupposes its specular character. Indeed, unless we are dealing with a phenomenon which is recognizable as a reflection over a wide range of settings of the crystal and whose position can be observed and stated with some precision, there can be no point in discussing the validity of any geometric formula

descriptive of it. No useful purpose would be served, for instance, in seeking to find empirically the point of maximum intensity in a field of diffuse scattering such as those represented theoretically in the curves of Fig. 3 of the preceding paper. The precision with which the positions of the X-ray reflections can actually be located and measured is an indication that the experimental situation in this respect is very different indeed from that arising in the case of X-ray scattering.

The earliest measurements made with diamond (Raman and Nilakantan, May 1940) showed that the spacing d^* of the dynamic stratifications altered rapidly with the setting of the crystal, being identical with the static spacing d of the (111) planes only at the particular setting when the two types of reflections appear superposed. It was found later that even these early measurements fitted perfectly into the general geometric law of quantum reflection

$$2\,d \sin\psi \sin(\vartheta \pm \epsilon) = \lambda \sin\vartheta, \qquad (1)$$

the angle ϑ coming out the same within a degree or two as the value of 54° 44′ established by the measurements over a wider range of settings of the crystal made in July and August 1940. The angle 54° 44′ is half the tetrahedral angle between the valence bonds joining the carbon atoms in diamond. It is also the angle between the faces of the cube and the octahedron in the regular crystal system. In other words, *the phase-waves for the quantum reflection of X-rays by the octahedral planes of diamond are parallel to the cube faces of the crystal.* This remarkable result which was discovered experimentally in September 1940 forms a striking confirmation of the basic ideas underlying the quantum theory of X-ray reflection. It emerged from the extended studies made in the preceding months as mentioned above. The photographs from which the measurements were made are reproduced in Plate XVII, Figs. 5 (*a*) to (*k*). A brief reference to this result was made in a footnote to the paper by Raman and Nath (November 1940) in which the theoretical formula (1) was first announced. The result itself was communicated in a letter to *Nature* dated the 11th November 1940 and published in its issue of the 25th January 1941. In view of the great significance and importance of the result, it appears worth while to give a detailed account of the experimental work which led to its recognition.

These early experiments were carried out with a 'Spektro Analyt' Rontgen apparatus manufactured by Siefert & Co., Hamburg. The X-ray tube was of the sealed hot-cathode type with a copper target, the X-rays emerging through four windows of Lindemann glass. The tubes worked at 41,000 k.v., with a tube current of 12 ma. A flat film type of camera was employed for taking the photographs. The X-ray beam was restricted by a

circular hole bored through cylindrical lead blocks of effective depth 93 mm., the diameter of the hole being 1·6 mm.

Diamond has a perfect cleavage parallel to an octahedral face of the cubic crystal. Plates evidently obtained by cleavage in this manner and subsequently polished can be readily obtained from jewellers in India. The plate actually used was about half a square centimetre in area with a thickness of 0·76 millimetre. The crystal was mounted on the goniometer with its faces nearly vertical and nearly normal to the X-ray beam. The crystal was set by trial so that the (111) planes within the crystal from which the reflections were to be studied were vertical, as also the adjoining lattice spacings parallel to the form of the cube. Thus, when the crystal was rotated about the vertical axis of the goniometer, the plane of incidence of the X-rays on the (111) spacings remained horizontal throughout, coinciding with a plane of symmetry of the crystal parallel to the form of the dodecahedron. Particular care was taken in mounting the crystal to ensure that the goniometer axis passed through the portion of the crystal irradiated by the X-ray beam. Small rotations of the crystal introduced no sensible change in the distance from the crystal to the photographic film. This however, was checked up at every setting of the crystal. The actual distance from the diamond to the film was 3·99 centimetres for Figs. 5 (*a*) to (*g*) and 3·95 cm. for Figs. 5 (*h*) to (*k*) in Plate XVII. With the aperture used, the X-ray beam traversing the diamond had an appreciable angular divergence. The round shape and sharpness of the spot as recorded on the film, however, enabled the position of its centre to be located with such accuracy that the use of a finer X-ray pencil would merely have prolonged the exposures necessary and thereby increased the difficulties of the investigation without any material gain in precision.

Since, in these experiments, the reflections occur in a plane of symmetry of the crystal, it follows that we may write the geometric law (1) in the form

$$2\,d \sin \tfrac{1}{2}(\theta + \phi) \sin\left(\vartheta \pm \frac{\theta - \phi}{2}\right) = \lambda \sin \vartheta \qquad (2)$$

θ and ϕ being the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Since the actual value of the crystal spacing is known, *viz.*, 2·056 A.U., the most convenient representation of the data is to regard the spacing as an unknown function of θ to be determined from the observed values of θ and ϕ and the formulæ used. The angle ϑ disappears from equation (2) when $\theta = \phi$. Thus, whatever be the chosen value of ϑ, the graphs representing the calculated values of the spacing as a function of θ calculated with different assumed values of ϑ all necessarily cross at the same point. This should agree with the known spacing of the crystal

within the limits of experimental error. When however, $\theta \neq \phi$, the spacing calculated would diverge progressively from the actual value unless the correct value of ϑ has been chosen. The appearance of the graph as a horizontal line in a position agreeing with the known crystal spacing thus furnishes an exact test of the formula employed.

Fig. 1 shows three graphs in which the experimental observations have been set out in the manner indicated. The graphs marked d_1 represents the

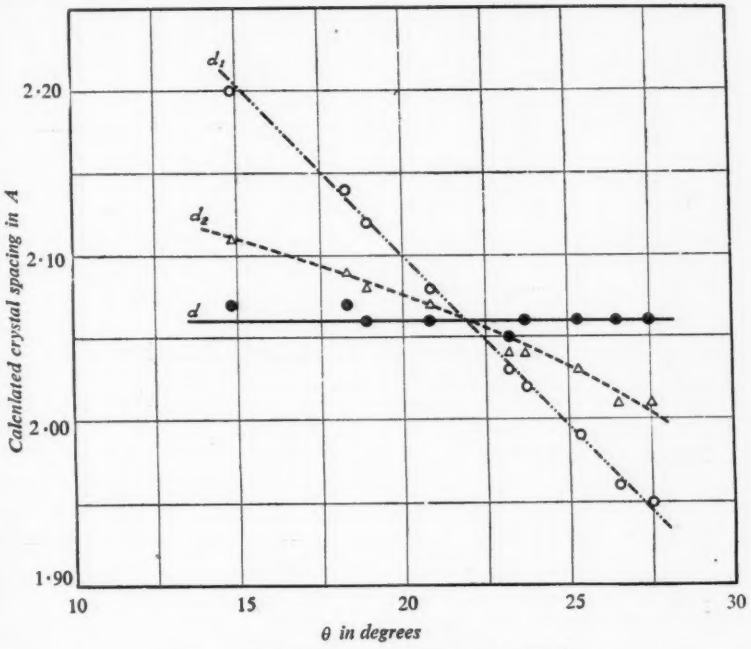

FIG. 1. Geometric Law of Quantum Reflection

crystal spacings calculated from the approximate formula

$$2\,d \sin \tfrac{1}{2}(\theta + \phi) = \lambda. \qquad (3)$$

The graph marked d_2 represents the crystal spacings calculated from the formula

$$d(\sin \theta + \cos \theta \tan \phi) = \lambda. \qquad (4)$$

This formula which is of the same form as that derived originally by Faxén on the basis of the scattering theory, would also represent the geometric formula of quantum reflection if the phase-waves of the infra-red lattice vibration had an arbitrary orientation within the crystal, and the actual

geometric position of the reflection were determinable from a consideration of the minimum phase wave-length. The graph marked d in the figure was calculated from the formula (2) above, assuming ϑ to be 54° 44′. It will be seen that it is a horizontal straight line with a spacing very closely agreeing with the known value. On the other hand, the graphs d_1 and d_2 diverge rapidly from the known spacing at except the point where all the three graphs intersect.

To indicate the degree of accuracy with which the angle ϑ is determinable from the observations, the graphs drawn for three different values of the angle are shown in Fig. 2. It will be seen that the angle lies certainly within one degree of half the tetrahedral valence angle.

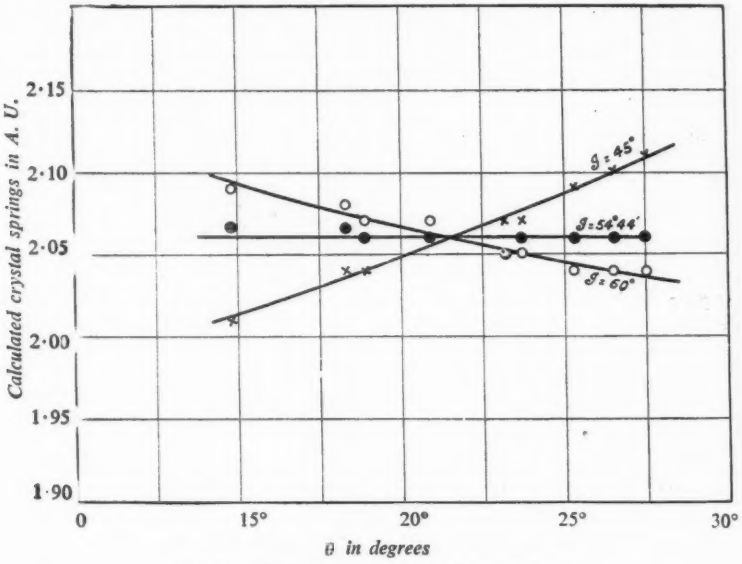

FIG. 2. The Inclination of the Phase Waves

The experimental facts emerging from Figs. 6 (*a*) and (*b*) in Plate XVIII, and from Figs. 1 and 2 above in the text are thus of a completely decisive character. The Debye-Faxén-Waller theory of X-ray scattering demands a distribution of the intensity of the scattered X-rays over an area whose angular extension is expressed in as many degrees of arc as the setting of the crystal is moved away from the position required for the classical X-ray reflection. It also demands that the position of maximum intensity in such scattering, though not capable of being measured with any particular precision, should follow the course of the curve marked d_2 in Fig. 1. On the other hand,

the actual spread of the quantum reflection is not experimentally detectable and if it is finite, is measureable in minutes of arc rather than in degrees, as indicated by Figs. 6 (*a*) and (*b*). The geometric direction of the reflection is capable of being determined with precision and follows a wholly different law, namely that defined by equation (2) above. The facts thus definitely negative any possibility of explaining the phenomena in terms of the Debye-Faxén-Waller theory. *The observed specificity of the value of ϑ also forms a direct experimental contradiction of the Born postulate of the cyclic lattice*, since the latter assumes the phase-waves of the vibration of the crystal lattice to have all possible orientations instead of a definitely restricted orientation as shown by the X-ray results. We have thus no choice left except that of assuming the infra-red or high-frequency vibrations of the lattice to be the factor responsible for the observed X-ray reflections.

We may now consider the question why the phase-waves of the 1332 vibration which are evidently responsible for the (111) reflections are parallel to the form of the cube. The answer to this is evidently that the nature of this vibration is determined by the geometry of the crystal structure. Each carbon atom in one Bravais lattice is joined by four valence bonds in a symmetrical fashion to four other carbon atoms belonging to the other Bravais lattice. The individual valence bonds are normal to the octahedral planes in diamond, while the planes parallel to the cube faces bisect the angles between the valence bonds taken in pairs. The vibration responsible for giving the reflection by a particular set of octahedral planes is normal to them and therefore parallel to one of the valence bonds. Since the three other bonds are also possible directions for such a vibration, it is to be expected that the plane of the phase-waves would take an intermediate direction, which by symmetry should bisect the angle between them. On the basis of this argument, it is evident that there should be three sets of possible phase-waves which are respectively parallel to the three pairs of faces parallel to the forms of the cube. This result demanded by considerations of symmetry is found as we shall see presently, to be fully supported by the experimental facts.

5. *The Azimuth Effect*

A further remarkable confirmation is forthcoming for the result that the phase-waves associated with the 1332 vibration are restricted to a specific crystallographic orientation. This is the so-called azimuth effect, which was foreseen theoretically before it was sought for and confirmed experimentally by the authors. Since the phase-waves for a (111) reflection are parallel to the adjoining cube face, it follows that if the crystal plate be rotated in its own plane so as to make the plane of incidence no longer a plane of symmetry of

the crystal, the quantum reflection should move out of such plane of incidence. Why this effect occurs becomes evident when we recall that the plane in which the quantum reflection should appear is the plane of incidence of the X-rays on the dynamic stratifications; in the circumstances considered, these are no longer perpendicular to the plane of incidence of the X-rays on the static crystal planes. This situation is readily appreciated with the aid of a vector diagram in which the reciprocals of the crystal spacing and of the phase-wave normal are geometrically represented. The point at which the phase-wave normal intersects the sphere of reflection necessarily moves out of the plane of incidence when the crystal is rotated in its own plane, the angle of incidence being retained constant. It is evident that such displacement would be zero if the reciprocal phase wave-length is zero; it changes sign when the direction of the wave-normal is reversed either by a change of the crystal setting or by a change of the X-ray wave-length. In other words, the displacement of the quantum reflection out of the plane of incidence would be zero when it coincides with the Laue reflection, and would be of opposite signs when it lies respectively on the two sides of it. It should also increase progressively as the quantum reflection moves away from the Laue spot in either direction. The theory of the effect has been very fully discussed and illustrated by appropriate diagrams in the paper by Pisharoty already cited. We need not therefore enter into the matter here in further detail. The necessary mathematical formulæ will be found in Pisharoty's paper. The effect is illustrated in Figs. 10 (*a*) and (*b*) in Plate XIX. The angular displacements of the reflections out of the plane of incidence as measured from the photographs are in quantitative agreement with those deduced from the formulæ.

6. *Explanation of Multiple Spots and Streamers*

Another striking confirmation of the theory of phase-waves is afforded by the phenomena arising from the fact that there are three sets of phase-waves and therefore three quantum reflections corresponding to the points where the phase-wave normals meet the sphere of reflection. As these normals are at right angles to each other, it is not to be expected that all the three reflections would be observable in every case. The setting of the crystal would obviously determine the effects actually recorded. It is evident that if the phase-wave vector nearly grazes the sphere of reflection, the finite divergence of the incident X-ray beam would result in the reflection appearing as an oblique streak or an elongated elliptic spot, instead of as a round circular spot; the latter would be the observed result only when the vector cuts the sphere of reflection normally. The intensity of the streamers or elliptic spots would vary with the reciprocal phase wave-length at each point,

being greatest when this is a minimum and tending to zero when it is large. Hence, these streamers and subsidiary spots would be most prominent when the setting of the crystal is such that the Laue and quantum reflections nearly coincide. On the other hand, when the quantum reflection is far removed from the Laue reflections, all trace of them should disappear. These effects are well illustrated as the series of photographs reproduced in Figs. 5 (*a*) to (*k*). A detailed discussion of them and of various other cases is given in the paper by Mr. Pisharoty already cited to which the reader may be referred for further particulars. Remarkable changes in the appearances of the streamers and subsidiary spots occur when the azimuth of the setting of the crystal is altered. Some of these features are illustrated in Figs. 10 (*a*) and (*b*) and 11 (*a*) and (*b*) in Plate XIX, and are in full accord with the indications of the theory.

7. *Intensity of Quantum Reflection*

Extremely rapid changes occur in the intensity of the quantum reflection as it approaches from the Laue spot with an alteration of the setting of the crystal. This effect is seen in the series of pictures reproduced in Figs. 5 (*a*) to (*k*) and is even more pronounced than would appear from the photographs since the exposures were considerably prolonged for the first few and the last few pictures of the series. A better idea of the situation is obtained from Fig. 7 which is reproduced from the article in *Current Science* for April 1940. It will be noticed that both the K_α and K_β reflections fall beyond the spot marked A and are so feeble as only just to be visible in the reproduction. The quantum reflection of K_α is beyond the spot marked C, while the K_β reflection actually coincides with the latter and therefore also with the classical monochromatic reflection. The spot marked C therefore appears very intense. The K_α and K_β quantum reflections appear respectively on the two sides of the spot marked B, the former being of great intensity. The illustration shows clearly that as the quantum reflection approaches the Laue spot, its intensity rapidly increases and ultimately becomes quite large.

It is evident from the pair of pictures appearing in Fig. 8 (*a*) and (*b*) that the intensity of the quantum reflection of the monochromatic X-rays may actually exceed the intensity of the Laue reflection by the same spacings of the white radiations accompanying the characteristic X-rays of copper. That the classical and quantum reflections of the same wave-length are of comparable intensity when they are superposed is indicated by the photographs reproduced as Figs. 11 (*a*) and (*b*) in Plate XIX. It will be noticed when the crystal is set so that the classical and quantum reflections coincide, the streamers emerging from the reflections on both sides are easily visible. Since these streamers are necessarily much weaker than the principal

quantum reflection, it follows that the latter should be comparable in its intensity with the classical reflection of the same wave-length which appears superposed on it. The experimental facts are thus in general accord with the conclusions arrived at from the quantum theoretical calculations set out in the preceding paper.

Experiments have also been made varying the thickness of the plate of diamond as also the width of the beam of X-rays used. These factors are found within wide limits to be without influence on the relative intensities of the classical and quantum reflections under otherwise similar conditions, thus supporting the indications of theory. On the other hand, the diffuse continuous background of scattered radiation appearing in the Laue patterns of diamond [*e.g.*, in Figs. 5 (*a*) to (*k*) and in Fig. 7] is practically suppressed by using thin plates or fine X-ray beams.

8. *Influence of High and Low Temperatures*

The spectroscope enables us directly to observe the changes of frequency in the scattered radiations which arise when energy and momentum are exchanged between a beam of light and the crystal which it traverses. The quantum-mechanical character of such scattering is indicated by the difference of the intensities of the radiations of increased and diminished frequencies respectively. The theoretical ratio of these intensities is simply the Boltzmann factor $e^{-h\nu^*/kT}$, actual measurements giving values closely agreeing with it. In the parallel X-ray problem, neither the spectroscopic observation of the change of frequency nor the comparison of the intensities of the two components ($\nu \pm \nu^*$) is at present possible. What we observe is the superposed effect of both components of frequency which, as shown in the preceding paper, is proportional to

$$\frac{e^{-h\nu^*/kT}+1}{e^{-h\nu^*/kT}-1}. \tag{5}$$

Measurements of the variation of intensity with temperature within the range for which the formula (5) may be expected to be valid should therefore enable us to demonstrate the quantum-mechanical character of the effects and to evaluate the frequency ν^* of the vibrations responsible for them in any particular case.

As shown earlier in this paper, the 1332 vibration is the only one which can be expected to give an appreciable variation of the structure amplitude of the (111) planes in diamond. It follows from this fact and from formula (5) that the intensity of the quantum reflection by the (111) planes should be sensibly independent of temperature. This result was indicated as a consequence of theory in the *Current Science* article of April 1940. In the more

detailed paper of May 1940, experiments were described in which the diamond was heated up to 500° C. without any notable enhancement of the intensity of the reflection resulting therefrom. Experiments at low temperatues were also indicated as a further test of the theory. A suitable high vacuum low-temperature X-ray camera suitable for quantitative work was then developed, and the tests made with it with the crystal cooled down to liquid-air temperature showed that the reflections continued to be visible at such temperatures. This was reported in a letter to *Nature*, dated the 20th September 1940 published in its issue of the 23rd November 1940. Further comparisons showed that the intensity of the reflections by the (111) planes at room and at liquid-air temperatures were practically identical. This result was communicated in a letter to *Nature* dated the 23rd November 1940 and published in its issue of the 25th January 1941.

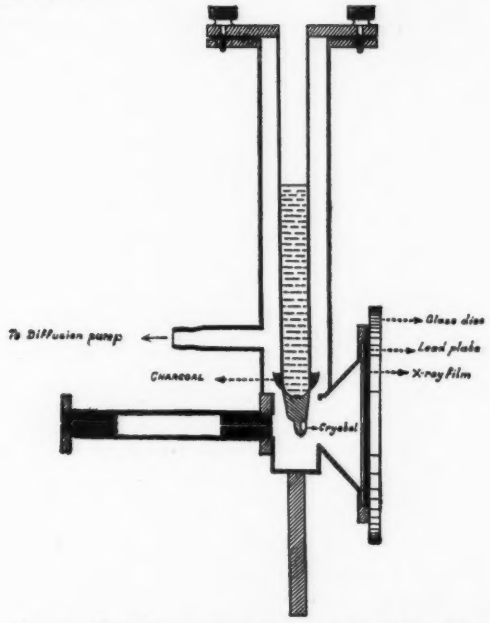

FIG. 3. High-Vacuum Low-Temperature X-Ray Camera

The special X-ray camera designed and constructed for the experimental study of quantum X-ray reflections at liquid-air temperatures is illustrated in Fig. 3 above. The diamond is imbedded in a copper block which forms the lowest end of the receptacle for holding the liquid air. A hole bored through the block allows passage for the X-ray beam. Both the crystal and the photographic film recording the X-ray pattern are held inside a high

vacuum, the latter being produced by an oil diffusion pump. No intensifying screen was used in these experiments. A small lead disc attached to the film served to cut off the central beam of X-rays. Photographs were taken under identical conditions with and without cooling the crystal by liquid air. Figs. 12 (*a*) and (*b*) in Plate XX, reproduce two typical photographs obtained in this way, the former at liquid air and the latter at room temperature. No sensible difference is noticeable in these photographs between the intensities of the quantum reflections appearing in the vicinity of the three Laue spots. Figs. 13 (*a*), (*b*) and (*c*) in Plate XX present a similar comparison of the intensities for the quantum reflections photographed under similar conditions at 25° and at 400° Centigrade. Here again, no difference in intensity is perceptible. The experimental results thus completely establish that the (111) reflections arise from a quantum-mechanical excitation of the infra-red vibrations of high frequency. It is important to notice that the reflections seen in Fig. 12 (*a*) are situated in the near vicinity of the Laue reflections. Accordingly, if the effects had arisen from elastic vibrations of the lattice, these would have been of very low frequency and would therefore have been totally suppressed by the cooling of the crystal to liquid air temperature.

9. *Quantum Scattering*

The diffuse halo surrounding the primary beam is a very striking feature of the Laue pattern reproduced in Fig. 7, the radiations here used being those of a copper target. Fig. 14 in Plate XXI reproduces a similar picture taken with the X-rays from a molybdenum target and shows a noticeable contraction of the halo, but not so great as should have resulted if the halo had been due entirely to the monochromatic X-radiations present. That the halo is not due solely or even principally to the scattering of the X-rays by elastic vibrations of *thermal origin* is shown by the fact that it persists at liquid air temperatures as seen in Fig. 12 (*a*) in Plate XX. Since the halo is recorded with the diamond inside a high-vacuum camera, it is evident that the effect cannot be due to the diffusion of the X-rays by the air. This is also otherwise clear from the fact, already mentioned, that the use of thin plates of diamond tends to supress the intensity of the halo in comparison with those of the regular reflections. We are thus obliged to conclude that the halo is a quantum mechanical effect, the X-rays exciting the vibrations of diamond lattice having much lower frequencies than 1332 and somewhat similar characters to the vibrations of an elastic solid. The extent to which the intensity of such scattering would be diminished by lowering the temperature would be greatest for the vibrations of the lowest frequency and least for those of the highest frequency. The intensity of the halo should therefore fall off in the close

vicinity of the direct beam, and remain sensibly unaffected in directions far removed from it. The distinct sharpening of the halo at low temperatures noticed on a comparison of Figs. 12 (*a*) and (*b*) is probably to be explained in this way. The outermost parts of the halo may reasonably be attributed to a diffuse scattering of the X-rays by the lattice planes of the crystal in combination with the elastic vibrations of the structure.

10. Summary

The paper presents the experimental evidence furnished by the X-ray studies with diamond which confirms the theoretical ideas and mathematical formulation contained in the two preceding papers. The nature of the vibrations of the crystal lattice of diamond is first discussed with special reference to the mode having a frequency of 1332 wave-numbers. This vibration gives a large variation of the structure amplitude of the (111) crystal planes, while other vibrations of a different character leave it unaffected. Various experimental tests show that the X-ray reflections of the second kind given by these planes are truly specular or geometric in character. Measurements of the geometric positions of the reflections over a wide range of crystal settings show a complete agreement with the theoretical formula, the phase-waves of the vibrations appearing parallel to the (100) planes of the crystal. Symmetry demands that there should be three such sets of phase-waves, and this is fully substantiated by the experimental facts. The quantum reflection moves out of the plane of incidence when the crystal plate is rotated in azimuth. The appearance of multiple spots and streamers is also explained by the theory. The intensity of the reflections is of the order of magnitude indicated by the theory and is sensibly independent of the temperature in agreement with it. The phenomenon of quantum scattering is also briefly described and discussed.

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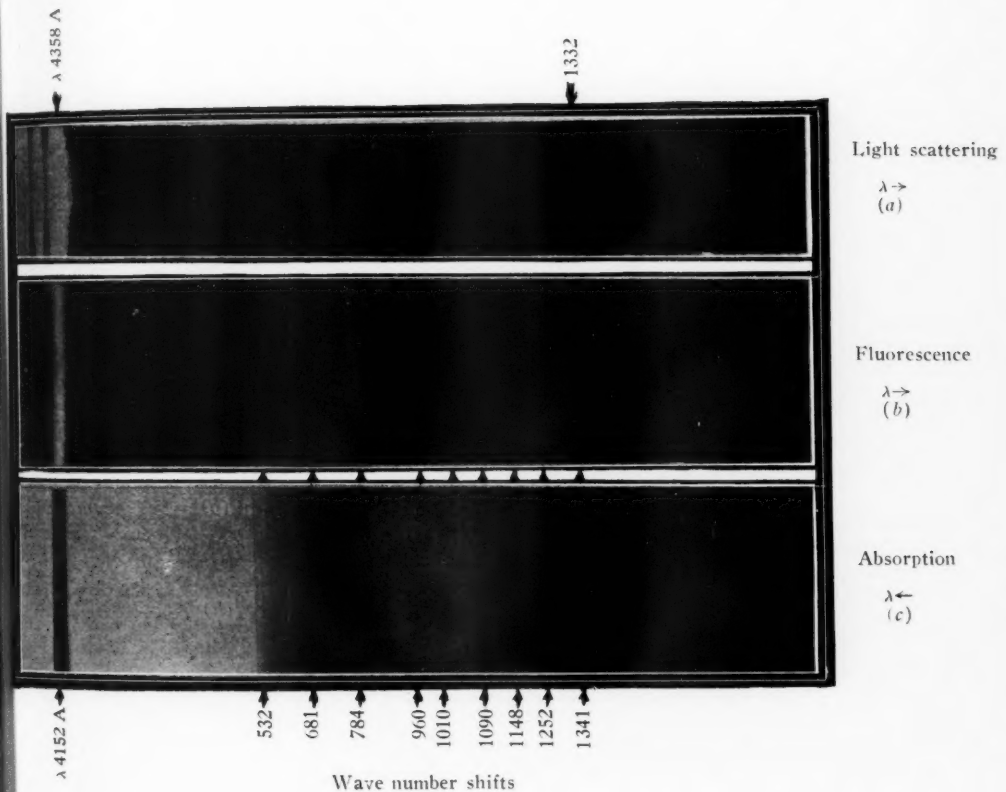


FIG. 4. Lattice spectrum of diamond appearing in (*a*) light scattering, (*b*) fluorescence, and (*c*) absorption.

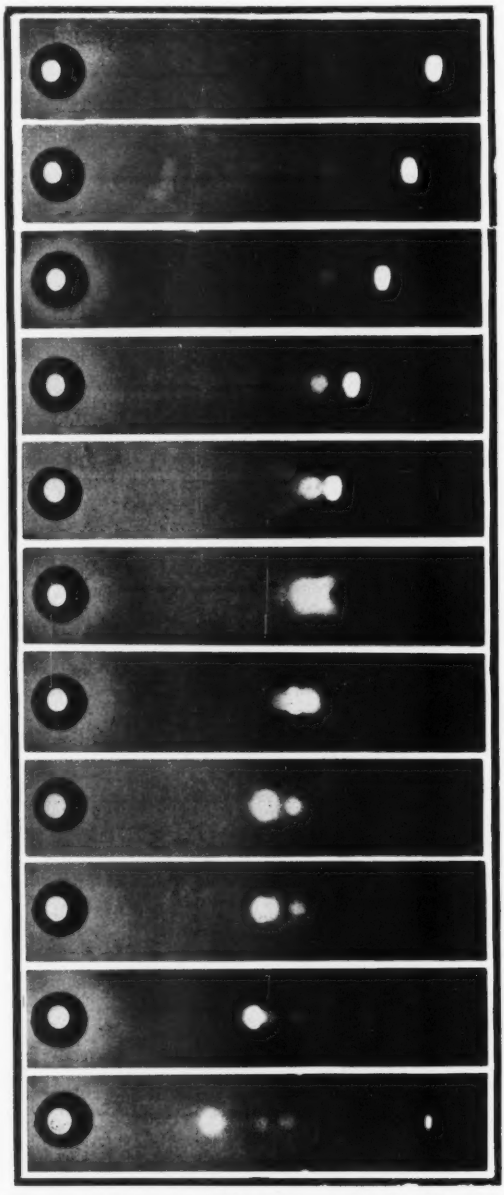


FIG. 5. Sequence of changes in (111) reflections with alteration of crystal setting

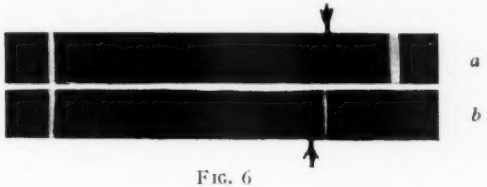


FIG. 6

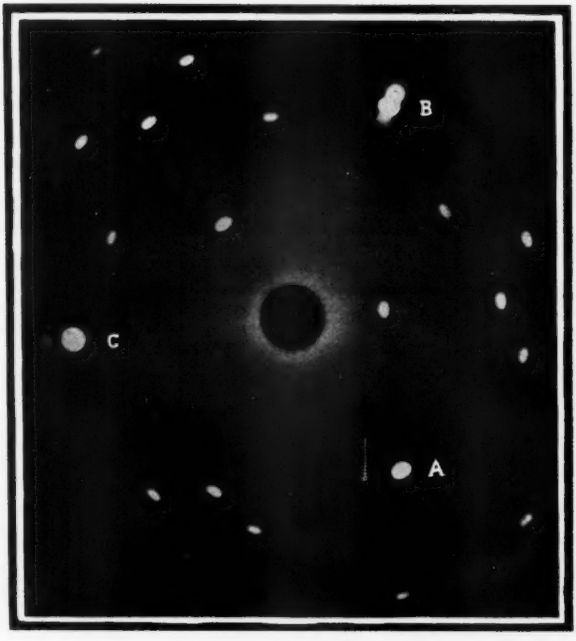


FIG. 7

FIG. 8

FIG. 6. Sharpness of quantum reflection.
FIG. 7. Spots, streamers and halo.
FIG. 8. Relative intensities of Laue and quantum reflections.

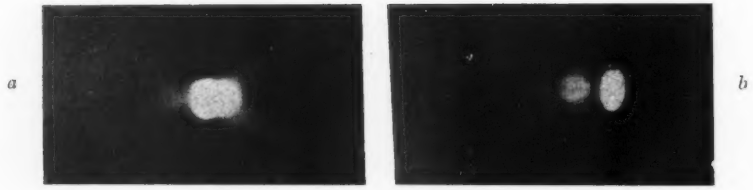


FIG. 9

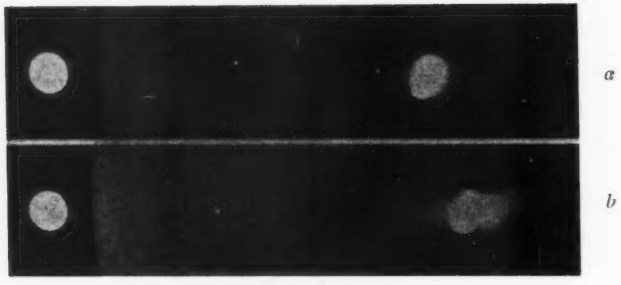


FIG. 10

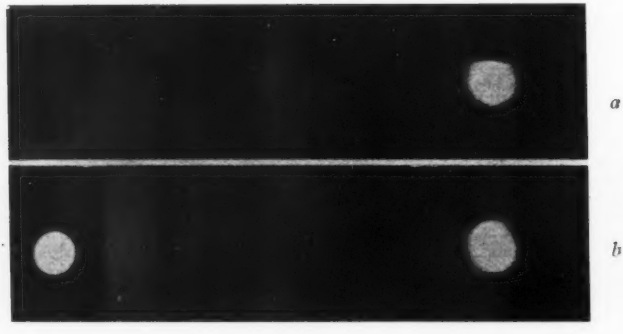
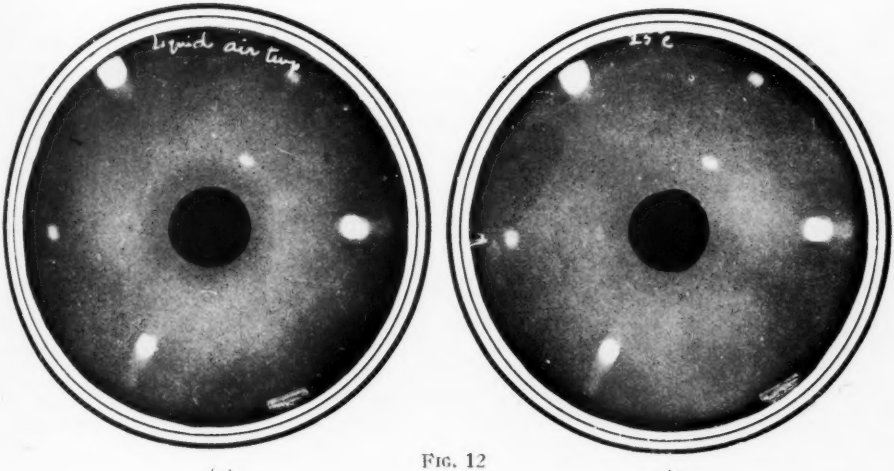


FIG. 11

FIG. 9. Spots and streamers.
FIG. 10. Azimuth effect.
FIG. 11. Superposition of classical and quantum reflections.



(a)
— 180° C.

FIG. 12

(b)
+ 25° C.

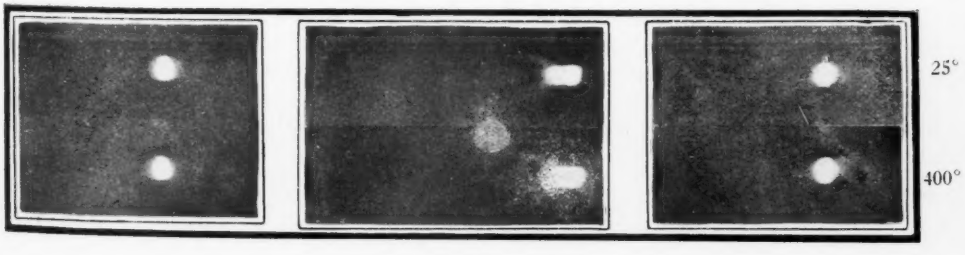


FIG. 13

FIG. 12. Quantum reflection and quantum scattering at (*a*), −180° C., (*b*) 25° C.
FIG. 13. Quantum reflections at + 25° C. and + 400° C.

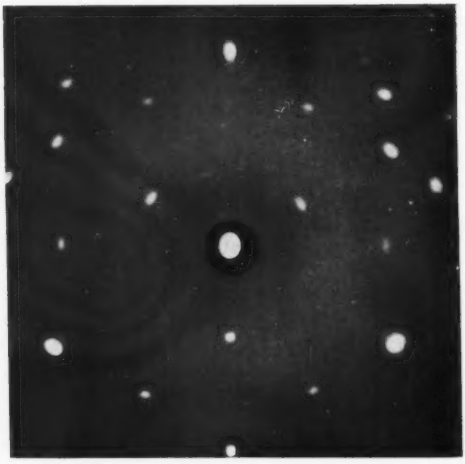


FIG. 14. Laue pattern of diamond with molybdenum radiation showing halo

A QUANTUM THEORETICAL EXPLANATION OF THE APPEARANCE OF FORBIDDEN X-RAY REFLECTIONS IN DIAMOND

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1. *Introduction*

When a narrow pencil of monochromatic X-rays is passed through a thin crystal, dynamic stratifications are excited in the crystal lattice and these give rise to the Raman or quantum X-ray reflections of altered frequency[1] which for the particular setting of the crystal at which they are most intense coincide in direction with the Bragg or classical reflections by the same crystal planes. The present paper deals with the calculation of the structure amplitudes of these dynamic stratifications in the particular case of diamond on the simple assumption that the incident X-rays impart to each degree of freedom corresponding to an infra-red oscillation of the lattice an energy equal to $h\nu^*$, ν^* being the frequency of the oscillation and h the Planck's constant. The simplicity of the structure of diamond and the well-known character of its Raman active, infra-red lattice oscillations, facilitates the calculation. Some of the planes which have zero structure amplitude for the classical Bragg reflections are shown to possess finite dynamic structure amplitudes for the Raman or quantum reflections, thus accounting for the appearance of the so-called "forbidden" reflections in diamond.

2. *Oscillations of the Diamond Lattice*

As is well known, a crystal of diamond can be pictured as built up either of two interpenetrating face-centred cubic lattices or of two interpenetrating rhombohedrons. On the former view the unit cell consists of eight atoms while on the latter it consists only of two atoms. Adopting the rhombohedral unit cell, Nagendra Nath[2] as well as Venkatarayudu[3] have derived identical expressions for the normal modes of oscillation of the diamond lattice and have shown that there is only one triply degenerate Raman active infra-red oscillation possible for the lattice. In other words, there are three degrees of freedom for the infra-red oscillations and another three for the elastic oscillations, making up the total of six degrees of freedom for the unit

cell of two atoms. We will adopt this point of view and take the Planck oscillator in diamond to consist of two atoms and be of frequency $3 \cdot 996 \times 10^{13}$ sec.$^{-1}$ corresponding to the shift of 1332 cm.$^{-1}$ wavenumbers exhibited by the intense Raman line.

3. *The Dynamic Stratifications Associated with the (111) Reflections*

The co-ordinates of the lattice points of a unit cell of diamond, referred to rectangular axes, are known to be

$$000;\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}0\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}0;$$

and

$$\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4};\ \tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4};\ \tfrac{3}{4}\tfrac{1}{4}\tfrac{3}{4};\ \tfrac{3}{4}\tfrac{3}{4}\tfrac{1}{4}.$$

Here the unit is 3·56 AU as obtained from the X-ray measurements. The structure amplitude F of the ($h\ k\ l$) planes is given by the formula

$$F = \sum_p f_p\, e^{2\pi i\,(hx_p + ky_p + lz_p)}, \tag{1}$$

where f_p is the atomic scattering factor of the pth atom whose co-ordinates are x_p, y_p, z_p.

When the atoms are at rest, the value of F for the (111) planes of diamond is given by

$$4 f_1 (1 - i),$$

where we take f_1, the atomic scattering power of the carbon atom, to be the same for all the atoms of the unit cell.

We will suppose that the incident X-rays excite the infra-red vibrations of the lattice in which one lattice vibrates against the other, the direction of vibration being assumed to be normal to the (111) planes. We are justified in this as we know from the Raman effect data for diamond that its intense infra-red oscillation is triply degenerate and since the oscillations parallel to the planes themselves have no influence on their structure amplitude. We further assume, as a limiting case, that all the unit cells vibrate completely in phase and that each cell is endowed with a quantum of energy $h\nu^*$, where ν^* is equal to $3 \cdot 996 \times 10^{13}$ sec.$^{-1}$, the observed frequency of the lattice oscillations in diamond.

The periodic displacement of the pth atom belonging to one of the lattices is given by

$$D_p = \mathbf{i}\, dx_p + \mathbf{j}\, dy_p\, \rho + \mathbf{k}\, dz_p \tag{2}$$

where

$$dx_p = a_p \sin (2\pi\ \nu^*\ t - \zeta) = d\ y_p = dz_p,$$

since the oscillation is normal to the (111) plane and all the atoms of one

lattice are in phase. The displacements of all the atoms of the other lattice are equal but opposite to those of the first.

If A be the amplitude of the oscillator taken along the [111] direction, we have

$$a = \frac{A}{\sqrt{3}}.$$

It is well known that the diamond lattice has three degrees of freedom corresponding to the elastic and another three corresponding to its infra-red, lattice oscillations. Hence each Planck oscillator composed of two atoms—one from each lattice—has an energy $h\nu^*$ associated with it. Therefore, if A be the amplitude of oscillation of one carbon atom and m its mass, we have

$$h\nu^* = \tfrac{1}{2}\,\Sigma\, mv^2 = 2 \times \tfrac{1}{2}\, m.\,(2\,\pi\,A\,\nu^*)^2$$

$$i.e., \qquad A^2 = \frac{h}{4\pi^2 m\,\nu^*}$$

$$\text{and} \qquad a^2 = \frac{h}{12\pi^2 m\,\nu^*}.$$

Substituting the values for h, m and ν^* we obtain,

$$a = 0{\cdot}0268 \times 10^{-8}\ \text{cm}. \tag{3}$$

We will calculate the structure amplitude of the dynamic (111) planes on the assumption that the atoms do not move appreciably in a time interval equal to the period of the X-ray vibration.

The co-ordinates of the vibrating atoms in a unit cell are

$$\left.\begin{array}{ll} \frac{dx}{u}, \frac{dy}{u}, \frac{dz}{u}; & 0+\frac{dx}{u}, \frac{1}{2}+\frac{dy}{u}, \frac{1}{2}+\frac{dz}{u}; \\ \frac{1}{2}+\frac{dx}{u}, 0+\frac{dy}{u}, \frac{1}{2}+\frac{dz}{u}; & \frac{1}{2}+\frac{dx}{u}, \frac{1}{2}+\frac{dy}{u}, 0+\frac{dz}{u}; \\ \frac{1}{4}-\frac{dx}{u}, \frac{1}{4}-\frac{dy}{u}, \frac{1}{4}-\frac{dz}{u}; & \frac{1}{4}-\frac{dx}{u}, \frac{3}{4}-\frac{dy}{u}, \frac{3}{4}-\frac{dz}{u}; \\ \frac{3}{4}-\frac{dx}{u}, \frac{1}{4}-\frac{dy}{u}, \frac{3}{4}-\frac{dz}{u}; & \frac{3}{4}-\frac{dx}{u}, \frac{3}{4}-\frac{dz}{u}, \frac{1}{4}-\frac{dz}{u}. \end{array}\right\} \tag{4}$$

and

Here $u = 3{\cdot}56$ AU—the side of a unit cell. Substituting these values in equation (1) and putting $h = k = l = 1$, we obtain

$$F_{111} = 4\,f_1 \left\{ e^{\frac{6\pi a}{u}\, i \sin(2\pi\nu^* t - \xi)} - ie^{-\frac{6\pi a}{u}\, i \sin(2\pi\nu^* t - \xi)} \right\}$$

We have the well-known relation

$$e^{i\alpha \sin \beta} = J_0(\alpha) + 2i J_1(\alpha) \sin \beta + 2 J_2(\alpha) \cos 2\beta + 2i J_3(\alpha) \sin 3\beta + 2 J_4(\alpha) \cos 4\beta + \ldots\ldots$$

where $J_n(\alpha)$ represents the nth order Bessel function of α.

Let us put

$$\frac{6\pi a}{u} = \alpha$$

and $(2\pi\nu^* t - \xi) = \beta$.

Then we obtain that

$$F_{111} = 4 f_1 (1-i) [J_0(\alpha) - 2 J_1(\alpha) \sin \beta + 2 J_2(\alpha) \cos 2\beta - 2 J_3(\alpha) \sin 3\beta + 2 J_4(\alpha) \cos 4\beta - \ldots\ldots]$$

The reflected radiation at a great distance ρ from the unit cell is given by

$$F e^{2\pi i (\nu t - \rho/\lambda)}$$

where ν is the frequency of the X-ray beam and λ its wave-length. Remembering that

$$\sin \beta = \frac{e^{i\beta} - e^{-i\beta}}{2i}, \text{ and } \cos \beta = \frac{e^{i\beta} + e^{-i\beta}}{2}$$

the expression for the secondary radiation becomes

$$\begin{aligned} & 4 f_1 (1-i) J_0(\alpha) e^{2\pi i (\nu t - \rho/\lambda)} \\ & \pm 4 f_1 (1+i) J_1(\alpha) e^{2\pi i \{(\nu \pm \nu^*) t - \xi_1\}} \\ & \pm 4 f_1 (1-i) J_2(\alpha) e^{2\pi i \{(\nu \pm 2\nu^*) t - \xi_2\}} \\ & \pm \ldots\ldots \end{aligned} \tag{5}$$

This means that the secondary radiation in the direction of the classical reflection consist partly of altered frequencies. Since α is small, terms containing $J_2(\alpha)$ and higher orders may be omitted. On quantum mechanical principles the intensity of the antistokes $(\nu + \nu^*)$ will be much smaller than that of the stokes $(\nu - \nu^*)$, so that the modified radiation consists practically only of $(\nu - \nu^*)$. The ratio of the structure ampltitude of this stokes' to that of the unmodified reflection is

$$\frac{J_1(\alpha)}{J_0(\alpha)} = 0{\cdot}071.$$

Thus in the correct Bragg setting of the crystal, these dynamic stratifications also are capable of giving a total reflection of the X-rays with modified frequency. But due to the phenomenon of 'extinction' for the primary beam in the correct setting of the crystal, the actual percentage of the modified reflection can never exceed about 7% of the total reflected intensity. Of course this can happen only when all the Planck oscillators are in phase—a limiting case.

4. *The Dynamic Stratifications Associated with the* (222) *Reflections*

Employing the values for the co-ordinates of the atoms given by the expression (4) and substituting $h = k = l = 2$, we obtain

$$F_{222} = 4f' \left\{ e^{i\,\frac{12\pi a}{u}\sin(\nu^* t - \xi)} - e^{-i\frac{12\pi a}{u}\sin(\nu^* t - \xi)} \right\},$$

where f' is the atomic scattering factor in the required direction.
Let us put,

$$\frac{12\pi a}{u} = \alpha' = 2\alpha$$

and $$(2\pi\nu^* t - \xi) = \beta$$

so that

$$F_{222} = 8f'\, i\, [2\, J_1(\alpha') \sin\beta + 2\, J_3(\alpha') \sin 3\beta + \cdots]$$

Hence the expression for the secondary radiation is

$$\begin{aligned} &\pm 8f'\, J_1(\alpha')\, e^{2\pi i\{(\nu \pm \nu^*)\, t - \xi_1\}} \\ &\pm 8f'\, J_3(\alpha')\, e^{2\pi i\{(\nu \pm 3\nu^*)\, t - \xi_3\}} \\ &\pm \ldots\ldots \end{aligned} \qquad (6)$$

We find that there can be secondary radiations of only modified frequency. In other words, if the atoms are at rest there can be no Bragg reflection at all. α' being small, Bessel functions of higher orders than the first can be omitted. The intensity of the antistokes $(\nu + \nu^*)$ being negligible in comparison with $(\nu - \nu^*)$, the (222) reflection will practically consist of X-rays of frequency $(\nu - \nu^*)$ and the structure amplitude of the spacings will be

$$8f'\, J_1(\alpha').$$

Its ratio to the structure amplitude of the static (111) spacings is

$$\frac{2f'\, J_1(\alpha')}{(1-i)f_1}$$

Taking the Hartee interpolation values for f' and f_1, the above ratio works out to be nearly 0·14.

It is well known that the (222) reflection in diamond is observed[4,5] in contradiction with the ordinary theory. It has been suggested[4] that this may be due to the two neighbouring carbon atoms of diamond being non-centro-symmetric regarding their scattering power. This hypothesis is supported neither by the calculations of L. Pauling[6] for the charge distribution in the carbon atom nor by the calculations of Hartee[7] for the scattering power of the atom. The above hypothesis is further contradicted by the non-appearance of the (200) reflection.

For a specimen of diamond behaving as an ideal crystal Ehrenberg, Ewald and Mark[5] estimate the intensity of the (222) Mo K_α reflection from a rotation picture about the (110) axis to be about a third of the (400) Mo K_β reflection. According to Hull the intensity ratio K_α: K_β for Mo is nearly 2·4. The above authors have found that the (400) reflection is about half as intense as the (111) reflection. Thus in their estimate the (222) reflection is about 0·07 times the (111) reflection.

For a perfect crystal the ' integrated reflection ' is proportional to

$$\frac{F\,(1+|\cos 2\,\theta|)}{\sin 2\theta} = F \cot \theta, \quad (\theta < 45°).$$

Hence the ratio of the (222) modified reflection to the (111) unmodified reflection would be

$$0{\cdot}14 \times \frac{\cot 20°}{\cot 10°} = 0{\cdot}068$$

for the Mo K_α radiation employed by those authors. This value is in excellent agreement with their observation. We may therefore reasonably infer that the (222) reflection actually observed is entirely a quantum or Raman reflection.

5. The Dynamic Stratifications Associated with the (220) *Reflections*

If we substitute $h = k = 2$, and $l = 0$ in equation (1) and use the co-ordinates of the atoms of the unit cell as given by the expression (4) we obtain for the structure amplitude of the dynamic (220) planes, the following expression:

$$F_{220} = 8 f_2 \cos \left\{ \frac{8\pi a}{u} \sin (2\pi \nu^* t - \xi) \right\}$$

$$= 8 f_2 \{ J_0(\alpha_1) + 2 J_2(\alpha_1) \cos 2\beta + 2 J_4(\alpha_1) \cos 4\beta + \ldots\ldots \}.$$

Here

$$\alpha_1 = \frac{8\pi a}{u}$$

$$\beta = (2\pi \nu^* t - \xi)$$

and f_2 is the corresponding atomic structure factor.

Hence the expression for the secondary radiation is

$$8 f_2 J_0(a_1) e^{2\pi i(\nu t - \rho/\lambda)} + 8 f_2 J_2(a_1) e^{2\pi i\{(\nu \pm 2\nu^*)t - \xi_2\}} + 8 f_2 J_4(a_1) e^{2\pi i\{(\nu \pm 4\nu^*)t - \xi_4\}} + \ldots\ldots \quad (7)$$

As before if we neglect the second and higher order Bessel functions of the small quantity a_1, we find that the (220) planes cannot give rise to any modified reflection of appreciable intensity. The failure of Dr. Nilakantan to record the (220) modified reflection in spite of a large number of trials is thus explicable.

6. The Dynamic Stratifications Associated with the (200) *Reflections*

According to the classical theory, the (200) reflection is another of the forbidden reflections in diamond. But the assumption of Planck oscillators excited by the incident X-ray quanta gives the following expression for the reflected radiation from these planes:

$$\pm 8 f_3 J_1(a_2) e^{2\pi i\{(\nu \pm \nu^*)t - \xi_1\}} \pm 8 f_3 J_3(a_2) e^{2\pi i\{(\nu \pm 3\nu^*)t - \xi_3\}} \pm \ldots\ldots \quad (8)$$

Here $a_2 = \dfrac{4\pi a}{u}$ and f_3 is the atomic scattering factor of the appropriate direction. This indicates a Raman reflection unaccompanied by any Bragg reflection. But the intensity of this modified reflection of frequency $(\nu - \nu^*)$—the others being negligible, can only be a third of the (222) reflection. In a rotation photograph about the (110) axis the number of the co-operating planes for the (200) reflection is only two while for the (222) it is four. Ehrenberg, Ewald and Mark[5] remark that in a rotation picture about the (110) axis the (222) reflection was just recorded while there was no indication of any (200) reflection. Their observation finds a ready explanation on this idea of lattice oscillations according to which the (200) spot has to be six times weaker than the weak (222) spot.

7. The Dynamic Stratifications Associated with the (662) *Reflections*

Since $h + k + l = (4n + 2)$ for this case, the (662) reflection is also 'forbidden' by the classical theory. Substituting these values of h, k and l

in (1) and using the co-ordinates given by expression (4), we obtain for the reflected radiation from the (622) planes the expression:

$$\pm 8 f_4 J_1(\alpha_3) e^{2\pi i\{(\nu \pm \nu^*)t - \xi\}}$$
$$\pm 8 f_4 J_3(\alpha_3) e^{2\pi i\{(\nu \pm 3\nu^*)t - \xi_3\}}$$
$$\pm \ldots\ldots \qquad (9)$$

Here $$\alpha_3 = \frac{28\pi a}{u}$$

and f_4 is the atomic scattering factor in the direction of this reflection.

The expression shows that there is no unmodified or Bragg reflection. Neglecting the ' antistokes' and the second and higher order Bessel functions the ratio of the dynamic structure amplitude of this reflection to that of the (222) reflection is

$$\frac{f_4 J_1(\alpha_3)}{f' J_1(\alpha')}.$$

The values of f_4 and f' of the carbon atom for the respective glancing angles of 60° and 10°, when Mo K_α radiation is employed, are found from the interpolation values obtained by the Hartee method and given in the " International Tabellen Zur Bestimmung Von Kristalstrukturen ". They are 0·8 and 1·8 respectively. Substituting these values and the values of α' and α_3, the above ratio works out to be nearly 0·9.

Since in a rotation picture the intensities of the spots on the equatorial line are proportional to

$$\frac{1 + |\cos 2\theta|}{\sin 2\theta} = \begin{matrix}\cot\theta \text{ when } \theta < 45° \\ \tan\theta \text{ when } \theta > 45°,\end{matrix}$$

the ratio of the intensity of the (662) to the (222) quantum reflection will be nearly

$$0{\cdot}9 \frac{\tan 60°}{\cot 20°} = 0{\cdot}57.$$

Ehrenberg, Ewald and Mark[5] remark that this ' forbidden ' (662) reflection does appear in a rotation photograph and that it is weaker than the ' forbidden ' (222) reflection; but they suggest a ratio 0·3. The discrepancy is not large when one remembers that these reflections are extremely weak and that the experimental value of the ratio of their intensities is only an estimate.

8. *Other Lattice Oscillations*

As mentioned in the Introduction we have here considered the rhombohedral unit cell having only one lattice oscillation which was identified as

that giving the Raman frequency of 1332 cm.$^{-1}$ The recent work of Nayar[8,9] on the luminescence and ultra-violet absorption spectra of diamond at low temperatures has revealed that the lattice spectrum of diamond contains a whole series of discrete frequencies ranging down to about 127 cm.$^{-1}$ Amongst these, 1332 and 780 appear most prominently and are the principal members of the two important groups of frequencies. Until these modes of vibration with lower frequencies are fully investigated and can be dynamically specified, it is not possible to discuss their influence on the dynamic structure amplitudes of the various crystal planes. It may be anticipated, however, that such influence should be relatively unimportant in respect of the lattice planes for which the 1332 oscillation is active. On the other hand, it is quite possible that for those planes for which the 1332 vibration is inactive, *e.g.*, the (220) planes, the lower frequencies may influence the structure amplitudes appreciably and give rise to dynamic reflections. If this were the case, such reflections would necessarily exhibit a more marked temperature dependence of intensity than the planes which are chiefly excited by the 1332 oscillation.

I am very much indebted to Sir C. V. Raman, F.R.S., for his kind and helpful guidance in the course of this work.

9. *Summary*

On the Raman idea of quantum exchanges of energy and momentum between a crystal lattice and an X-ray photon traversing it, the dynamic structure amplitudes of the various crystal planes of diamond are worked out assuming that each Planck oscillator takes up one quantum of infra-red vibrational energy from the incident X-rays. It is shown that such an interaction gives rise to X-ray reflections of altered frequency in most cases. The structure amplitude of the (111) planes for this modified or Raman reflection is found to be about 7% of that of the same planes for the Bragg reflection. The (222) planes, the (200) planes, and the (662) planes, the Bragg reflections from which are 'forbidden' according to the classical theory, are found to possess finite structure amplitudes for the quantum reflections. The values of these structure amplitudes are shown to quantitatively account for the intensities of the reflections appearing from these planes as recorded by Ehrenberg, Ewald and Mark. It is therefore suggested that the so-called 'forbidden' reflections which appear in diamond are pure Raman or quantum reflections of modified frequency.

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LOW-TEMPERATURE STUDIES OF THE RAMAN X-RAY REFLECTIONS IN CRYSTALS

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1. Introduction

Early in 1940, Sir C. V. Raman and Dr. P. Nilakantan made the very significant discovery that the (111) planes of the crystal lattice in diamond give a second kind of monochromatic X-ray reflection which is as truly geometric as the usual Bragg reflection, being quite as sharply defined, but having evidently a different origin since it is observable over a wide range of settings of the crystal and obeys a different geometric law. The observed characters of this reflection indicated that it represents the X-ray analogue of the well-known Raman effect observed in the scattering of light. In other words, the X-ray photon falling upon the crystal excites the high frequency or infra-red vibrations of the crystal lattice, the latter deriving their energy from the incident X-rays. The appearance of the X-ray photon of diminished energy as a geometric reflection by the lattice planes is accounted for on the very reasonable assumption that the infra-red vibrations are excited simultaneously in all the lattice cells of the crystal with such phase relations as to give rise to a coherent effect. It follows from these considerations that if the primary X-ray frequency is ν, the reflected X-rays have a frequency $(\nu - \nu^*)$, ν^* being the frequency of the excited infra-red vibrations of the crystal.

It is well known from the Raman effect studies on the scattering of light in crystals that in general, both "Stokes" $(\nu - \nu^*)$ and "anti-Stokes" $(\nu + \nu^*)$ radiations are observed in the spectra, their absolute intensities being respectively proportional to

$$\frac{1}{1 - e^{-h\nu^*/kT}} \text{ and to } \frac{1}{e^{h\nu^*/kT} - 1}$$

and their relative intensity being accordingly $e^{h\nu^*/kT} : 1$. When $h\nu^* \gg k\mathrm{T}$, it is evident that only the component of diminished frequency would be present. On the other hand, when $h\nu^* \ll k\mathrm{T}$, the two components tend to be of equal intensity. In the case of diamond, the observed facts indicate that the infra-red vibrations excited by the X-rays are the same as those giving the strong Raman line at 1332 cm.$^{-1}$ Since therefore, $h\nu^*$ is much greater than $k\mathrm{T}$ at the ordinary temperature, it

follows that in the case of diamond we are only concerned with X-rays reflected with *diminished* frequency. It follows also, as indicated by the formulæ, that the intensity of the reflection should then be sensibly independent of temperature. This indication of theory was confirmed by Raman and Nilakantan in their earliest experiments by heating the diamond to a few hundred degrees above the room temperature, no marked increase of intensity being then observed. They also suggested as a test of the theory, the study of the effect of cooling down the diamond to liquid air temperature. This test was carried out by them a few months later; the results which were in entire accord with the theory were briefly reported at the time (1940). A more detailed description of the full technique of the investigation appears in a paper by Raman and Nilakantan elsewhere in these *Proceedings*.

It is obviously of great interest to supplement the investigations on diamond by similar researches with other crystals at low temperatures. It is evident that, in general, we would have quantum or Raman X-ray reflections of both *diminished* and *increased frequencies* superposed on each other. The observed intensity of the modified reflection should then be the sum of the two expressions quoted above. In other words, the actual intensity of the quantum reflection would be proportional to

$$\frac{e^{h\nu^*/kT} + 1}{e^{h\nu^*/kT} - 1}.$$

At sufficiently low temperatures, this expression reaches the limiting value unity. On the other hand, at sufficiently high temperatures, it asymptotically tends to the value $2\,kT/h\nu^*$, thus becoming proportional to the absolute temperature. It is evident also that the ratio between the limiting intensity at low temperatures and the values reached at higher temperatures would depend on the frequency of the infra-red vibrations of the crystal excited by the X-rays. The higher this frequency, the more nearly would the intensity tend to remain constant throughout the whole range of temperature. On the other hand, when the frequency ν^* is low, we should have to go down to liquid air temperatures or even lower before the limiting intensity is reached.

It is evident from the foregoing remarks that the study of the quantum or Raman X-ray reflections gives us a method of investigating the infra-red spectrum of crystals from a new point of view, which should obviously prove of great importance. It should also be remarked that the study of the intensity curves of the modified reflections and their comparison with the variation to be expected theoretically from the known infra-red frequencies of the crystal, would furnish an experimental confirmation of the nature of these reflections as quantum or Raman reflections of modified frequency and

indeed enable us to determine by a thermodynamic method the actual changes of frequency occurring in such reflections. To emphasize this aspect of the matter, the present investigation has been carried out with a series of four crystals whose infra-red frequencies are in descending order of magnitude, *viz.*, carborundum, sodium-nitrate, rock-salt and penta-erythritol.

2. *Experimental Arrangements*

The X-ray camera used for taking the Laue photographs at low temperatures is constructed essentially on the principles developed by Nilakantan and is illustrated in Fig. 1. The crystal C is mounted in a cavity at the end of a copper rod R fixed to the bottom of the inner tube of a cylindrical metal Dewar flask D and carefully pressed into metallic contact by thin copper foils and a screw ring E. $S_1 - S_2$ is the lead-slit system which is fixed to the camera B in such a way that the narrow beam of X-rays emerging from it passes through the centre of the crystal, and falls on the photographic film. The film adapter P is screwed on to the flange-end of the camera and an aluminium flat A is fixed at the end by pressing it home with high-vacuum putty. The lead slit S_1 is rendered vacuum tight by a thin aluminium foil. A high vacuum is maintained in the camera throughout the exposure by means of an oil diffusion pump. One fill of the tube D with liquid air lasts for half an hour; but during the exposure, the level is made up every fifteen minutes. The exposure is started only half an hour after the crystal is cooled down to the liquid air temperature, thus ensuring the crystal being at that temperature from the start of the exposure. In photographing the spectra, an intensifying screen is not used, as it was found that the latter becomes a serious source of error in the measurement of the intensities of spots. The X-ray generator is a demountable Coolidge tube with a Mo-anticathode and operated at 45 K.V. and a fairly steady milliamperage of 25 m.A. Laue photographs exhibiting the Raman reflections are taken at the room temperature for the same time of exposure under identical experimental conditions. Their relative intensities are measured microphotometrically making use of a density-log. intensity curve and for the same mode of development as that employed for the other

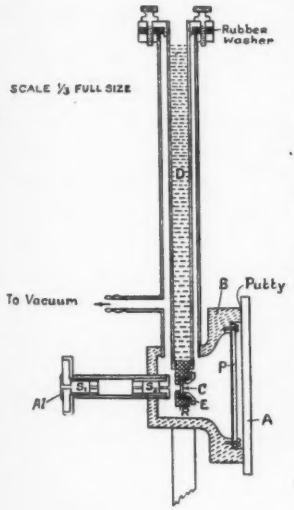

FIG. 1
Low-temperature high-vacuum X-ray camera

films obtained for the molybdenum radiations. In the case of rock-salt, photographs were also taken for the temperature of solid carbon dioxide and the relative intensities obtained microphotometrically were checked up by those got by an alternative method of varying the time of exposure till the intensities of the spots at the two temperatures are equal. If t_1 and t_2 are the times of exposure at the two temperatures T_1 and T_2, the ratio of intensities $I_1/I_2 = (t_2/t_1)^n$, where n is the Schwarzchild constant which is found experimentally to be nearly unity for the X-ray film and the radiations used. Considering the limitations of the experimental method, the possible error in the values will be as high as 10%. The photographs with carborundum were also obtained at 600° T and 900° T using for the purpose an electrical heater of nichrome wire, and their intensities were compared with that obtained at the room temperature for the same setting of the crystal.

3. The Experimental Results and their Significance

Figs. 2 *a-h* in the accompanying Plate illustrate the Laue patterns obtained with carborundum, rock-salt, sodium nitrate and penta-erythritol. It will be noticed that in every case the reflections persist at the liquid air temperature. The corresponding Laue reflections exhibit an enhanced intensity which is the greater when the diminution of intensity of the Raman reflections is most marked. This clearly indicates that the temperature dependence of the intensity of the Bragg or the Laue reflections can only be correctly explained when their relation to the Raman reflections from the same crystal planes is taken into account.

In Fig. 3, the intensities of the Raman reflections at the different temperatures as compared with that given at the liquid air temperature by the

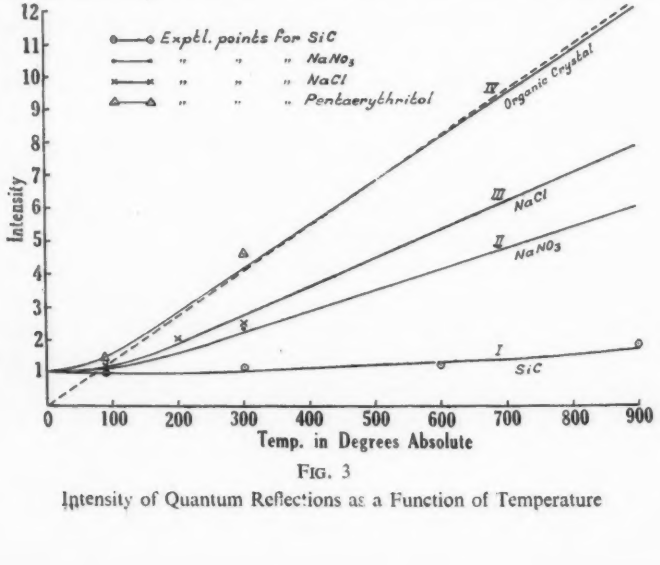

FIG. 3

Intensity of Quantum Reflections as a Function of Temperature

theory taken as the standard, are plotted along side the theoretical curves of intensities obtained in accordance with the equation given earlier and with appropriate frequencies chosen for each case (see Table I).

TABLE I

Crystal	T^0	90	200	300	600	900
	$kT \times 10^{-13}$	12·3	27·4	41·1	82·2	123
Carborundum $\nu^* = 800$ cm.$^{-1}$	$\frac{h\nu^*}{kT}$	12·9	5·8	3·9	1·94	1·3
	Intensity (Theo.)	1	1·006	1·042	1·34	1·77
	Intensity (Exp.)	1	..	1·1	1·3	1·82
Rock-salt $\nu^* = 160$ cm.$^{-1}$	$\frac{h\nu^*}{kT}$	2·58	1·161	·774	·387	·258
	Intensity (Theo.)	1·163	1·9	2·72	5·3	7·9
	Intensity (Exp.)	1·163	1·93	2·43	..	..
Sodium nitrate $\nu^* = 200$ cm.$^{-1}$	$\frac{h\nu^*}{kT}$	1·65	·74	·5	·23	·165
	Intensity (Theo.)	1·073	1·588	2·209	4·125	6·128
	Intensity (Exp.)	1·073	..	2·36	..	..
Penta-erythritol $\nu^* = 100$ cm.$^{-1}$	$\frac{h\nu^*}{kT}$	1·65	·74	·5	·23	·165
	Intensity (Theo.)	1·48	2·82	4·08	8·14	12·1
	Intensity (Exp.)	1·48	..	4·59	..	..

Carborundum.—The carborundum crystal used in the investigation is a clear plate of nearly 1 mm. thick and the Laue photograph shows that it belongs to the hexagonal type. The X-rays were incident nearly normal to the cleavage face. The Raman reflection appears in close proximity to the Laue reflection as a *round* spot which is fairly intense. The reflection shows only a small increase of intensity as the temperature is raised from 90° T to 900° T. This suggests that the infra-red frequency active in the Raman reflection of X-rays is relatively high. According to Schaefer and Thomas (1923), the hexagonal type of carborundum crystal shows only one strong sharp infra-red

reflection at 12 μ (830 cm.$^{-1}$) which they assume as the fundamental frequency for SiC. Accordingly, Curve 1 in Fig. 3 is drawn assuming that the Raman frequency associated with the modified spot is nearly 800 cm.$^{-1}$ It will be noticed that the experimental points all fall in the neighbourhood of this curve, indicating that the frequency change involved in the reflection is the same as the characteristic infra-red frequency.

Rock-salt.—The Laue photographs of a thin plate of rock-salt are obtained for 90°, 194° and 300° T with X-rays nearly normal to the 100 plane. A lowering of the temperature is accompanied by a change of intensity of the modified reflections which approximately fits in with a frequency of 160 cm.$^{-1}$ for the active infra-red vibration as shown by Curve 3 in Fig. 3. Rock-salt has only one rest-strahlen frequency at 52 μ (192 cm.$^{-1}$) and its Raman spectrum obtained by Fermi and Rasetti (1931) shows two fairly intense lines at 160 and 350 and at least two other weak diffuse maxima between 200 and 300 cm.$^{-1}$. In a separate paper, the vibrations of the sodium chloride lattice are analysed and the X-ray active mode of vibration is indicated. The results of the present investigation show that the frequency of this vibration is in the neighourhood of 160 cm.$^{-1}$ In addition to a diminution of intensity, a slight sharpening of the Raman reflections is also noticeable at the liquid air temperature. This observation is of great theoretical significance, but the exact extent of sharpening can be ascertained only by using a linear slit and the reflection method for photographing it.

Sodium nitrate.—The Laue patterns reproduced in Figs. 2 *e* and *f* show the strong Raman reflections from the 211 plane of a crystal of sodium nitrate very near the Bragg setting in addition to other weak reflections. The relative intensities of this spot at 90° and 300° T plotted in Curve 2, Fig. 3 show agreement with a vibrational frequency of nearly 200 cm.$^{-1}$ The Raman spectrum of sodium nitrate yields two intense lattice frequencies at 98 and 185 cm.$^{-1}$ (Nisi, 1932; Nedungadi, 1938) and thus the latter is to be taken as the active vibration in the modified reflection of X-rays by the 211 plane. Raman and Nilakantan (1940) observed that if the temperature is raised to 280° C., the modified reflection of X-rays from the 210 plane gains rapidly in intensity with a corresponding fall in intensity of the Laue reflections. This observation taken in conjunction with the results obtained here suggests that the active frequency for these two planes may be different. The temperature studies of intensity of the modified reflection from various crystal planes thus affords a method of detemining the mode of vibration which varies the structure amplitude of any plane to the maximum extent.

Penta-erythritol.—This crystal is chosen as the representative of organic crystals of which the lattice is molecular and the units are held together by

weak van der Waals forces. The intensity of the modified reflection is considerably diminished at 90° T and is nearly one-third of that at 300° T, being thus nearly proportional to the absolute temperature. In view of this marked diminution of intensity at the liquid air temperature, it is not surprising that Lonsdale, 1940 (see Preston, *Nature*, 1941) failed to observe the same in organic crystals especially as the pattern obtained by her at the lower temperature is masked by the intense halo of liquid air. From the measurements of relative intensities made up to 90° T, it is not possible to obtain even the roughest estimate of the infra-red frequency in this case. We could however, conclude that this frequency should be less than 100 cm.$^{-1}$ as shown by Curve 4 in Fig. 3. The dotted curve by its side shows what the rate of fall would be if it were proportional to the absolute temperature. This conclusion regarding the Raman-active lattice vibration in modified X-ray reflection by organic crystals is in agreement with the experimental observation in the Raman effect that a large variety of these crystals yield discrete lattice oscillations with a frequency range of 25–120 cm.$^{-1}$ (Venkateswaran, 1938).

General Remarks.—The present investigation thus clearly demonstrates that the determination of the rate of change of intensity of the modified X-ray reflection with temperature provides a new method of obtaining the infra-red spectrum of crystals. The frequency of vibration could be estimated fairly accurately by measurements made at the room temperature and at liquid air temperature if it falls in the region 250–500 cm.$^{-1}$ For frequencies below 250 cm.$^{-1}$, temperatures lower than 90° T will have to be employed to obtain the same degree of accuracy. The method promises to be particularly suitable for crystals for which the methods of light scattering and the infra-red absorption or reflection are not applicable.

In conclusion the author wishes to express his heartfelt thanks to Sir C. V. Raman, F.R.S., for his suggestions and keen interest in the work.

Summary

The Raman reflections of X-rays by carborundum, rock-salt, sodium nitrate and penta-erythritol are obtained at liquid air temperature with a specially designed vacuum X-ray camera and their intensities are compared with those at room temperature. For rock-salt an intermediate temperature of solid carbon dioxide and for carborundum two higher temperatures namely 600° and 900° T have also been employed. From the relative intensities of these reflections at various temperatures, the infra-red frequency active in the particular reflection is ascertained in each case making use of the following formula

Intensity $\propto \frac{e^{h\nu^*/kT}+1}{e^{h\nu^*/kT}-1}$. These frequencies are about 800 cm.$^{-1}$ for carborundum, 160 cm.$^{-1}$ for rock-salt, 200 cm.$^{-1}$ for sodium nitrate and less than 100 cm.$^{-1}$ for penta-erythritol. They coincide with one or other of the low frequencies observed in the Raman effect or in the infra-red spectrum of the respective crystal. This new X-ray effect thus provides a novel method of evaluating the infra-red frequencies of crystals and is specially suitable for substances for which the methods of light scattering and infra-red spectroscopy are inapplicable.

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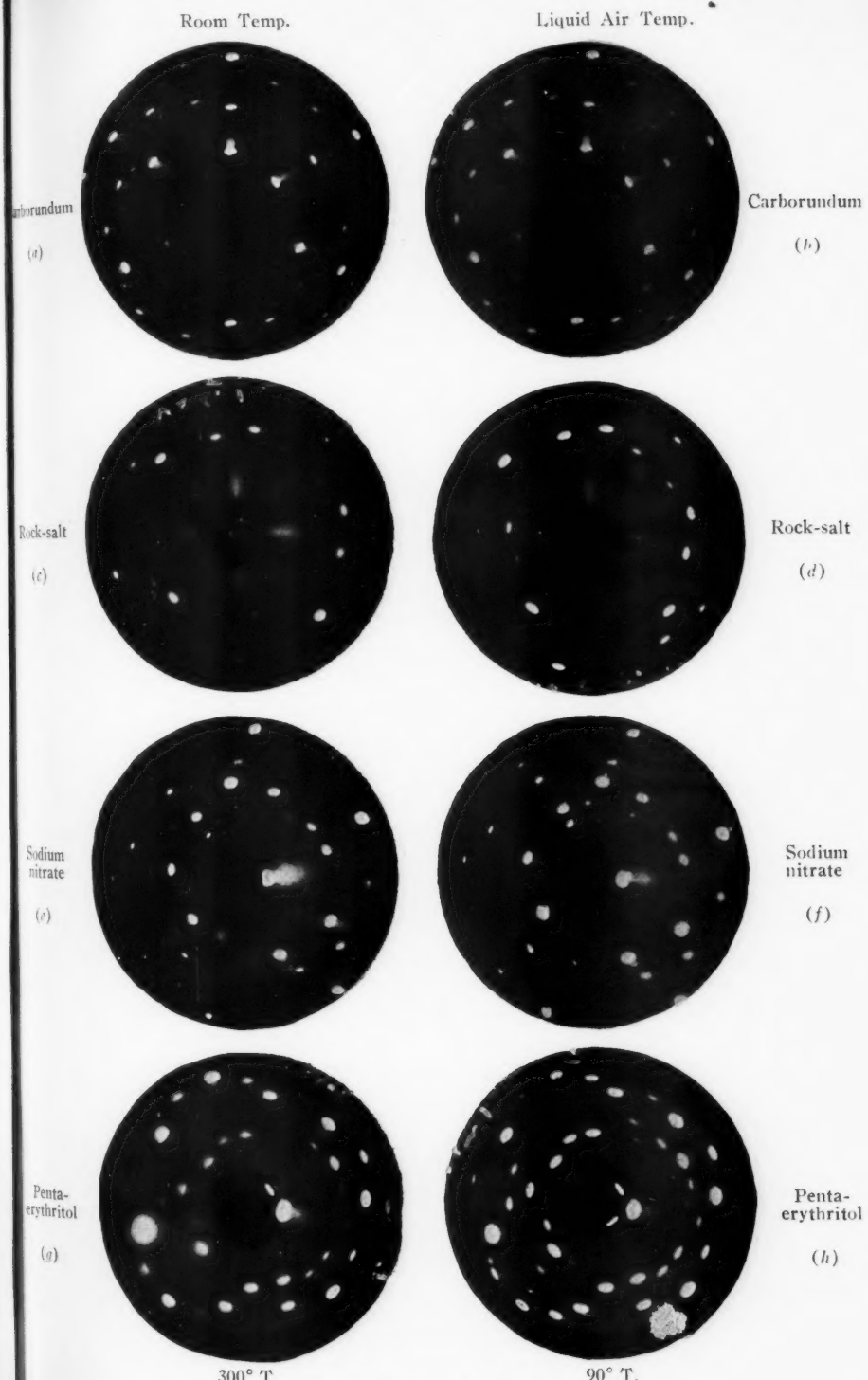

FIG. 2. Raman X-ray reflections in crystals

THE QUANTUM REFLECTION AND THE QUANTUM SCATTERING OF X-RAYS IN ROCK-SALT

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1. Introduction

During the past year numerous papers have appeared concerning the origin of the diffuse spots and streaks observed by Wadlund[1] (1938) in well-exposed Laue photographs of rock-salt crystal. On the basis of their original observations on the sharply defined monochromatic X-ray reflections shown by the (111) planes of diamond over a wide range of the crystal settings, Raman and Nilakantan[2] (1940) put forward the view that the diffuse spots observed in rocksalt have also a similar origin, namely that they are due to a *reflection of the X-rays with a change of frequency* arising from the quantum mechanical excitation of the infra-red vibrations of the crystal lattice. About the same time Zachariasen[3] (1940) put forward the view that the Faxen[4]-Waller[5] (1923) theory of temperature-scattering of X-rays by crystals explains the phenomenon. This point of view has been supported by Preston,[6] Lonsdale[7] and Born[8].

In a paper in the course of publication in this *issue*, Sir C. V. Raman[9] has theoretically examined the effect of the atomic vibrations in a crystal on the X-rays traversing it, starting from certain classical considerations originally put forward by Laue[10], and has arrived at the following general conclusions: (1) The infra-red or high-frequency vibrations of a crystal lattice are quantum-mechanically excited by the incident X-ray photons; as the result of the periodic variation of the structure amplitude of particular crystal planes resulting from such vibrations, the incident monochromatic X-rays are reflected by the crystal planes with a change of frequency. *These dynamic or quantum reflections are quite distinct from the static or unmodified reflections*, except that at the Bragg setting of the crystal they coincide with the latter in direction. The direction in which the dynamic reflection appears at other settings of the crystal is determined by the inclination of the phase waves to the crystal planes. (2) The elastic or low-frequency vibrations of the crystal give rise to diffuse maxima of scattering of the kind postulated in the Faxen-Waller-Zachariasen theory.

At the Bragg settings of the crystal, the maxima are sharpest, then coinciding with the regular reflections by the lattice planes. But they fall off rapidly in intensity and become much more diffuse when the glancing angle is altered in either direction. The formulæ indicate that the direction in which the hump of scattering intensity is to be expected alters with the crystal setting roughly—but by no means exactly—in the same way as the quantum reflection by the same lattice planes. (3) In addition to this, there is a general scattering of X-rays of the Brillouin type forming a diffuse cone round the primary beam, their change of frequency being dependent on the angle of scattering. The second and the third effects due to the *elastic waves in the crystal* come under what may be called the *quantum scattering of X-rays*. The relative intensity of the quantum scattering to the quantum reflection would depend upon various factors, including especially the structure of the crystal, and the temperature of observation.

The present investigation was undertaken with the object of examining the origin of the diffuse spots observed with rock-salt by some simple experimental tests capable of deciding between the alternative theories which have been proposed.

2. *Influence of the Volume of the Irradiated Crystal*

It is well known that as a result of the primary and secondary extinctions, the number of layers of a crystal effectively taking part in the Laue or Bragg reflections is limited to an extent depending upon the degree of its crystallographic perfection. The increase of the thickness of the crystal beyond such limit results only in the loss of the intensity of reflection due to the absorption by the medium traversed. From the preliminary considerations set forth above it will be evident that a similar situation should also exist in respect of *the quantum or Raman reflections of the X-rays*. In other words, the ratio of the intensity of a Raman spot in a Laue pattern to that of any of the Laue spots due to *approximately the same X-ray wave length* should remain the same irrespective of the thickness of the crystal plate used or the narrowness of the incident beam, other things remaining the same. The size of the spots due to the quantum reflections should also increase with the area and the thickness of the crystal traversed by X-rays and with the divergence of the incident beam in much the same manner as for the Laue spots.

The situation is, however, very different for the *quantum scattering* of X-rays of either of the kinds described above. The "extinctions" restricting the number of layers in the case of a reflection do not enter into consideration and therefore, the intensity of the quantum scattering should be

proportional to the volume of the crystal irradiated except for the diminution due to absorption which arises also for the Laue or the Raman reflections. Thus, by taking a series of Laue photographs with different thickness of crystal and with varying widths of the X-ray beam traversing it, we should be in a position to decide whether we are dealing with a true reflection or a simple scattering by the crystal planes.

3. Experimental Results

Figs. 1, 2 and 3 in the accompanying Plate illustrate the Laue patterns obtained with molybdeneum radiations incident normally to the 100 planes of rocksalt of thickness 0·5 mm. and 0·25 mm. respectively cleaved from the same block of a natural crystal. The diameter of the pin-hole used for the front lead slit was 1·32 mm. for Figs. 1 and 3 and 0·4 mm. for Fig. 2, which gave for the area of the crystal illumined 5·1 and 0·86 sq. mm. respectively. Since the intensity of the incident X-rays is diminished by the reduction of the size of the pin-hole, the time of exposure is suitably increased for the fine pin-hole in order to record the patterns with not too widely differing intensities. In comparing Figs. 1 and 2, it should be noted that the thickness of the crystal and the width of the incident beam are both different, the volume of the crystal irradiated being in the ratio 12: 1 as between the two cases. The ratio of the intenstiy of the transmitted beam to that of the incident beam, I/I_0, for five wave-lengths is tabulated below from the known absorption data for rock-salt :

Thickness of Crystal	λ in A.U.	·417	·497	·631	·710	·88
·25 mm.	I_1/I_0	·915	·865	·75	·665	·49
·50 mm.	I_2/I_0	·84	·748	·559	·45	·32
	I_1/I_2	1·09	1·09	1·32	1·48	1·53

It will be seen from the table that the effect of absorption is small up to 0·5 Å. The effect of the absorption for the softer X-rays as between the crystals of different thickness can be made out from the patterns reproduced in Figs. 1 and 2. At the same time, it is clear that the relative intensity of the Laue spots and the diffuse maxima in the two photographs is practically unaltered in spite of the fact that the volume of the crystal irradiated for Fig. 2 is only one-twelfth of that for Fig. 1. Figs. 2 and 3 are reproductions of the Laue patterns obtained with identically the same crystal and the same setting, only the size of the pin-hole and the exposure time being varied. Although the Laue pattern in Fig. 3 is more intense than in Fig. 2, a microphotometric comparison of the intensity of the diffuse spot

due to the Mo·K_α rays with that of the weak Laue spots in the neighbourhood shows only an increase of intensity of the order of about 10% for Fig. 3 in spite of the irradiated volume on the crystal being increased nearly six-fold. It may also be noticed on comparing Fig. 2 with either Fig. 1 or 3 that the increased diameter of the pin-hole and the divergence of the incident beam produce very similar effects on the lateral extension of the Laue spots and the "diffuse maxima". These experimental facts conclusively prove that the intensity of the extra spots or streaks observed with rock-salt are in the main not proportional to the irradiated volume but are determined by considerations of the same kind as the intensity of the Laue or Bragg reflections. If there is any true volume scattering, it is less than one-tenth of the observed effects in its intensity.

4. The Intensity and Sharpness of the Dynamic Reflections

In the theoretical paper by Raman already referred to, it has been shown that the intensity I of the scattering at an angle 2ψ due to the elastic vibrations of the crystal is given by

$$I \propto \frac{\sin^2\vartheta}{\sin^2\epsilon} = \left\{1 + \frac{\sin^2\theta_B}{\sin^2\psi} - 2\,\frac{\sin\theta_B}{\sin\psi}\cdot\cos\,\epsilon\right\}^{-1}$$

where θ_i is the angle of incidence, θ_B the Bragg angle, ϑ the inclination of the elastic wave-fronts to the crystal plane and $\epsilon = \psi - \theta_i$. Since

$$\cos\,\epsilon = 1 - 2\sin^2\epsilon/2 = 1 - 2\,(\epsilon/2)^2\ ;$$

$$I \propto \left\{\left(1 - \frac{\sin\theta_B}{\sin\psi}\right)^2 + \frac{\sin\theta_B}{\sin\psi}\cdot(\epsilon)^2\right\}^{-1} \qquad \text{(I)}$$

This corresponds to the factor

$$\cos^2(\theta_B - \psi)\,[1 + 2\cos^2\psi]/(\Delta\,\sin 2\,\theta_B)^2$$

in Zachariasen's modified formula[11] (1941) and tends to make the intensity infinity for small values of ϵ (or Δ*). As will be seen by the curves given later in Fig. 4, it also gives an asymmetrical distribution of the intensity and a shift of the maximum towards the Laue spot as in the case of the latter. But it has the added advantage that it remains valid for values of ϵ up to 20°.

In order to find whether the "diffuse maximum" in rock-salt falls off in intensity in the manner indicated by the above expression, the intensity distribution of the diffuse spots due to the 1st, 2nd and 3rd order reflections of the (200) plane of rock-salt have been determined microphotometrically from

* $\Delta = \theta_i - \theta_B$.

the same Laue photograph. A very narrow beam of X-rays emerging from a pin-hole of diameter of 0·4 mm. and having a divergence of 30′ is let fall on the 100 planes of a rock-salt crystal, 0·42 mm. thick, at a glancing angle of 19°·49′. For this setting of the crystal, the maxima due to the first three orders are recorded with comparable intensities. The time of exposure is so chosen that the " maxima " are recorded with just sufficient intensity to give deflections in the microphotometer yielding a value between 0·3 and 0·6 for the log-intensities. The density-log. intensity curve for molybdenum radiations experimentally obtained was observed to be a straight line in this region and covers a range of intensity of about 1 : 20. Accuracy of measurement was thus ensured.

The graphs *a*, *b* and *c* in Fig. 4 are drawn with 2ψ for the abscissæ and the intensities as ordinates for the three orders. Curve 1 gives the intensity

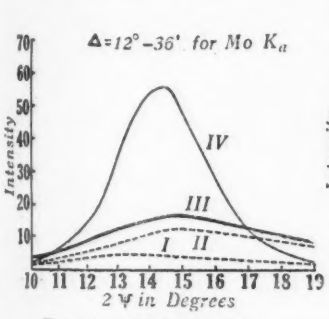


FIG. 4 (*a*) 200 Reflections from Rock-salt

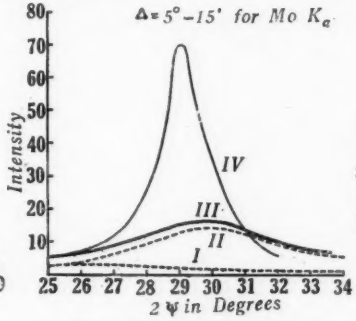


FIG. 4 (*b*) 400 Reflections from Rock-salt

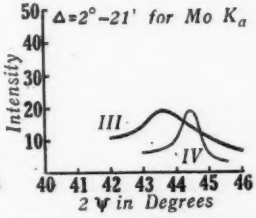


FIG. 4 (*c*) 600 Reflections from Rock-salt

distribution due to molybdenum K_β obtained by making use of formula 1 and reduced to 40% corresponding to its relative intensity to K_α; curve 2 is that due to K_α, and curve 3 gives the sum of the two intensities. The formula takes into account the increased scattering in the higher orders of reflection. In plotting the intensities of 1st, 2nd and 3rd orders to the same scale, the calculated values were reduced in the ratio 100 : 19 : 4·87 respectively. Thus, the curves 3 in Fig. 4 *a*, *b* and *c* indicate the relative magnitudes of the intensities of the three orders and the nature of their distribution to be expected if formula I holds. Curves 4 give the observed form of distribution, the peak intensity of the 3rd order being made equal to its theoretical maximum. From a study of the curves the following conclusions may be drawn:

The half-widths obtained from the theoretical curves 3 for the 1st, 2nd and 3rd orders and measured in a direction opposite to the central spot are

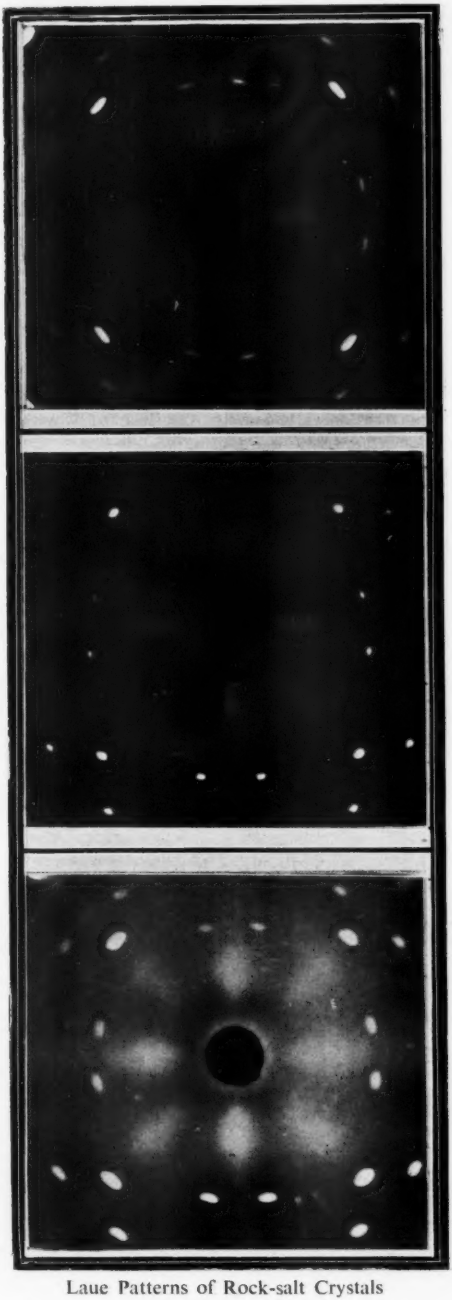
3°·24′, 2°·42′ and 1°·40′. The corresponding values obtained for K_α only from the simplified formula of Zachariasen[3] (*viz.*, $\Delta \sin 2\theta_B$) are 2°54′, 2°·33′ and 1°·40′ respectively. On the other hand, the experimental data obtained from curves 4 in Fig. 4 are 1°·50′ for the 1st, 1° for the 2nd and 35′ for the 3rd order. It must be remarked that the finite divergence of the incident beam only tends to make the experimental values somewhat higher. For regions in the close neighbourhood of the Bragg setting ($\Delta = \pm 60'$), the theoretical half-widths calculated from the simplified formula are more than 70% higher than the experimental values furnished by the careful experiments of Zachariasen and Siegel[12] (1940). The modified formula recently given by Zachariasen[11] (1941) also gives a higher value for the half-width.* Thus we may conclude that the Raman reflections in rock-salt are much sharper than is indicated by the formula $\frac{\sin^2/\vartheta}{\sin^2/\epsilon}$. Secondly, it may be seen from the curves 3 in Fig. 4 that if the peak intensity of the 3rd order is taken as unity, that of the 1st and 2nd orders should be 0·9 and 0·85 respectively. On the contrary, the observed peak intensity of the 1st order is 2·9 times and that of the second order 3·7 times these theoretical values, showing thereby that the fall of intensity of the spot with increasing values of ϵ is much less rapid than is represented by the above formula. These experimental facts clearly demonstrate that neither as regards the variation of half-width of the spot nor of its intensity with crystal orientation, do the so-called " diffuse maxima " in the Laue pattern of rock-salt obey the laws appropriate to the scattering of X-rays by the elastic vibrations of the thermal origin in the crystal.

In conclusion the author expresses his sincere gratitude to Sir C. V. Raman, Kt., F.R.S., N.L., for his stimulating interest in the work.

5. *Summary*

The ' diffuse maxima ' in the Laue patterns of rock-salt are obtained for two different crystal thickness and two different sizes of the pin-holes in the lead slit; the ratio of the volumes of the crystal irradiated by X-rays in the two cases being nearly 1 : 6 and 1 : 12. A comparison of their intensity with the weak Laue spots in the same pattern does not show any appreciable change due to the increase of the volume of the crystal. It is also noticed that the increase of the diameter of the pin-hole and the divergence of the X-ray beam has the same effect on the shape and dimensions of the Laue

* The half-widths given by curves I and II in Fig. 4 in the paper by Zachariasen (1941) are for a pin-hole and give therefore only the lower limit for the linear slit used by Zachariasen and Siegel.



Laue Patterns of Rock-salt Crystals

FIG. 1

Crystal thickness 0·5 mm.
Area illumined 5·1 sq. mm.

FIG. 2

Crystal thickness 0·25 mm.
Area illumined 0·86 sq. mm.

FIG. 3

Crystal thickness 0·25 mm.
Area illumined 5·1 sq. mm.

spots and of the diffuse maxima. A microphotometric study of the intensity distribution of the 1st, 2nd and 3rd order spots due to the (200) planes of rock-salt reveals that they are much sharper and that the fall of intensity for increased angles of reflection is much less rapid than is to be expected if they were due to the scattering of X-rays by the thermally excited elastic waves in the crystal. It is therefore concluded that these diffuse maxima in rock-salt are due mainly to the *quantum or Raman reflections* of the X-rays due to the excitation by the X-ray quanta of the monochromatic or infra-red vibrations of the crystal lattice.

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THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: I. NAPHTHALENE

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1. Introduction

One of the most remarkable and significant facts in crystal physics brought to light by recent investigations is the appearance of monochromatic vibrations of very low frequency as a very general feature in the lattice spectra of crystalline solids. The Raman spectra of practically all crystals, both of the inorganic and the organic class, and of the most varied type, *e.g.*, elements, ionic and molecular lattices, exhibit lines with low frequency shifts. These lines (of which there may be several) appear with the solid, often with notable intensity and sharpness, but disappear or else are replaced by a continuous spectrum when the substance melts or passes into solution. The literature of the subject has been reviewed by the author[1] in a paper in the Raman Jubilee Volume (1938) where studies of the phenomenon in several organic crystals are also described. The origin of these low frequency lines is now well understood to be due to the oscillations of the atoms, ions, or molecules in the lattice with respect to one another, such oscillation being either hindered translations or hindered rotations according to circumstances. Such vibrations being of low frequency, they are strongly excited by thermal agitation and appear with both diminished and increased frequency in the spectra. Simple considerations indicate that a large proportion of the thermal energy of the solid, especially in organic crystals where there are several molecules in the unit cell, must be taken up by such low frequency monochromatic vibrations. It is also evident that such vibrations would powerfully influence the structure amplitudes of the lattice planes and hence must play a notable part in determining the effects resulting from the passage of X-rays through the crystal.

Considering the experimental facts stated above and also the theoretical ideas developed by Sir C. V. Raman in a paper appearing earlier in these

Proceedings, it follows that the passage of X-rays through an organic crystal should result in the excitation of the specific modes of vibration having these low frequencies and hence also in a dynamic reflection of the X-rays by the lattice planes whose structure amplitudes are varied by such vibrations. Further, the character of these reflections, *viz.*, their intensity, geometric direction, sharpness and their temperature variations should exhibit the closest correlation with the geometry, frequency and amplitude of these modes of vibration. As the frequencies of these modes are usually low (30 to 100 cm.$^{-1}$ in spectroscopic units), their intensity should show a strong temperature dependence, diminishing rapidly with a fall of temperature, but reaching a limiting value at the lowest temperatures. A study of the typical case of pentaerithrytol from this point of view has already appeared in an earlier paper by the present writer in these *Proceedings*. In order to illustrate other aspects of the subject, a detailed study has been made of three cases, *viz.*, naphthalene, benzophenone and urotropin, in which we have a detailed knowledge both of the crystal structure and also of the low frequency infra-red vibrations from the studies of their Raman spectra.

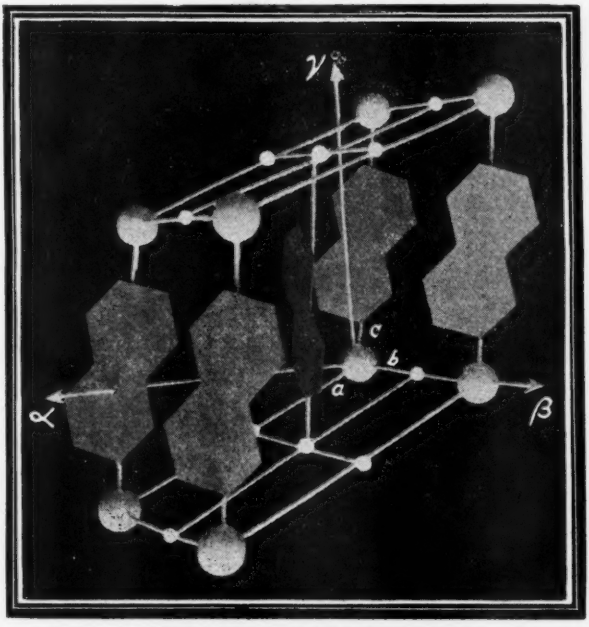

FIG. 7. Crystal Model of Naphthalene

2. *Crystal Structure and Lattice Spectrum of Naphthalene*

Naphthalene $C_{10}H_8$ belongs to the monoclinic prismatic class in the space group C_{2h}^5. The unit cell has the dimensions $a = 8{\cdot}29$, $b = 5{\cdot}95$ and $c = 8{\cdot}68$ Å and $\angle\beta = 122° 42'$ (Bragg,[2] 1921; Banerji,[3] 1930; and Robertson,[4] 1933) and contains 2 molecules of $C_{10}H_8$. The molecule consists of two fused benzene rings lying in a plane. The orientation of the molecules in the crystal is illustrated in Fig. 7* taken from a paper recently published by Nedungadi. The long axis of the molecule makes angles of $\phi = 115°{\cdot}3$, $\psi = 102°{\cdot}6$ and $\omega = 28°{\cdot}7$ and the short axis $\phi' = 71°{\cdot}2$, $\psi' = 28°{\cdot}8$, $\omega' = 69°{\cdot}1$ respectively with a, b and c' axes (c' is perpendicular to a and b) of the crystal. The orientation of the second molecule in the centre of unit cell is given by the glide plane reflection of the corner molecule in the 010 plane, the glide plane being parallel to the 'a' axis. The above crystal structure of naphthalane is in agreement with the magnetic and optical anisotropies observed in the crystal.

The molecule of naphthalene belongs to the symmetry class D_{2h} (Kohlrausch,[5] 1935; Bonino,[6] 1936; Saxena,[7] 1938) and has 48 normal modes of internal vibration, 24 of which are active in the Raman effect and 20 in the infra-red. In the crystal these internal vibrations of the two molecules in the unit cell presumably remain the same, as is shown by the identity of the Raman spectrum of the substance in the liquid and in the crystalline state (Nedungadi,[8] 1941). The total of twelve degrees of rotational and translational freedom of the two molecules together, give rise to the lattice oscillations and the Debye elastic waves in the crystal, *nine* of them being assigned to the former and *three* to the latter. Thus it is clear that the elastic vibrations would contribute only a relatively small part of the thermal energy of the crystal at the room temperature. Since the crystal possesses a low order of symmetry, the nine lattice oscillations are most probably all non-degenerate. In the Raman spectrum of naphthalene crystal, four lines have been observed (Gross and Vuks,[9] 1935, 1936; Venkateswaran,[1] 1938; and Nedungadi,[8] 1941) which have to be definitely attributed to the lattice vibrations. Fig. 8 in the accompanying Plate reproduces the spectrum of a single crystal of naphthalene photographed by Nedungadi. As the frequencies are low, they are thermally excited at the room temperature as is shown by the almost equal intensities for the Stokes and anti-Stokes Raman lines in the spectrum.

3. *Dynamic X-Ray Reflections in Naphthalene*

The X-ray analogue of the Raman effect in naphthalene was studied by Bhagavantam and Bhimasenachar[10] (1941). They observed the dynamic

* In Fig. 7, α, β and γ are the axes of the optical polarisability ellipsoid.

X-ray reflections by 001, 002 and $20\bar{1}$ planes of naphthalene, but these were recorded only when the crystal orientations were nearly the same as those required for the static reflections. For other orientations and other planes they were unable to observe the spots presumably because the source of X-rays used by them was not sufficiently strong. The more powerful equipment available at this Institute has made a thorough investigation possible. A thin plate of naphthalene crystal, prepared from a solution of a mixture of alcohol and water, is mounted on a goniometer with the 001 (cleavage) plane lying in a vertical plane. The source of X-rays was a demountable self-rectifying filament X-ray tube with copper anti-cathode and run at 25 mA and 45 kilo-volts. As the crystal sublimes rapidly, a series of twelve Laue photographs were taken in succession with an exposure time of half an hour in each case. Figs. 1 and 2 in the accompanying Plate are the patterns obtained with the incident beam making a glancing angle of $6°\cdot45'$ and $11°\cdot42'$ with the 001 plane, being thus very near the Bragg angles for the first order ($6°\cdot5'$) and for the second order ($12°\cdot7'$) reflections from that plane for the copper K_α radiations. It may be noticed that the static reflections are recorded with great intensity in both the photographs. But there is only a faint indication of the dynamic reflection of the first order in either case. In Fig. 1, the second order dynamic reflection is recorded weakly as a diffuse spot in the same line as the central spot and the 001 Laue spot. At the same time the *weak* Laue spot in a direction making an angle of nearly 120° with the 001 Bragg reflection, is accompanied by a *strong* dynamic reflection. In Fig. 2, the latter is very close to the Laue spot showing that the crystal is very near the Bragg setting for the corresponding crystal plane. From the distance of this spot from the centre and the intensity of the Bragg reflection and the setting of the crystal, the plane is identified as $0\bar{1}1$ plane. Figs. 3–6 are taken with the crystal rotated both about the vertical and horizontal axes. It may be observed that several crystal planes give rise to Raman reflections. For the normal incidence on the 001 plane of naphthalene, the X-rays are making a glancing angle of $4°\cdot15'$ with the $20\bar{1}$ plane, which varies only slightly as the crystal is rotated about a vertical axis. Thus in Figs. 3 and 4, for which the 001 plane lies in a vertical plane, the angles of incidence of the Laue spot due to $20\bar{1}$ plane, which may be observed vertically above the central spot, are $4°\cdot59'$ and $4°\cdot44'$. The crystal planes corresponding to the other dynamic reflections could be identified from their position on the plate, the angle they make with $20\bar{1}$ reflection and with each other and the known orientation of the crystal.

Table I gives the indices of these planes, the glancing angles* of incidence θ_i and the angle of reflection $(\theta_i + \phi)$, the spacing d calculated from the relation, $2d \sin \frac{(\theta_i + \phi)}{2} = n\lambda$ for the Raman reflection, the estimated intensity

TABLE I

No.	Indices of Plane	Ref. to Fig.	θ_i	$\frac{1}{2}(\theta_i + \phi)$ for Kα	Lattice Spacing in A.U.		Intensity (Dynamic)	Intensity (Static)	
					Experimental	Calculated		Bragg	Robertson F′
1	001	1	6°·45′	..	..	..	w.	v.st.	27·5
		2	11°·42′	5°·55′	7·476	7·3	v.w.	,,	,,
2	002	1	6°·45′	12°·9′	3·65	3·65	,,	..	15·5
		2	11°·42′	..	..	..	w.	..	,,
3	$0\bar{1}1$	1	12°·50′	9°·33′	4·63	4·66	v.st.	0	6
		2	11°·0′	9°·33′	,,	,,	,,	..	,,
4	110	3	6°·54′	9°·40′	4·52	4·58	st.	st.	37
5	$11\bar{1}$	4	11°·12′	9°·27′	4·68	4·63	med.	med.	..
6	120	3	17°·42′	16°·30′	2·7	2·77	w.	..	12·5
7	$20\bar{1}$	3	4°·59′	10°·46′	4·115	4·12	med.	st.	40
		4	4°·44′	10°·33′	4·2	,,	,,	,,	,,
		5	8°·32′	,,	,,	,,	,,	,,	,,
		6	14°·51′	,,	,,	,,	,,	,,	,,
8	$21\bar{1}$	3	13°·56′	12°·52′	3·45	3·39	,,	,,	..
		4	7°·22′	..	..	..	v.w.	..	..
		5	7°·56′	12°·48′	3·47	3·39	med.	st.	..
9	$20\bar{2}$	5	6°·11′	12°·28′	3·56	3·72	,,	..	21·5
		6	11°·18′	,,	,,	,,	,,	..	,,
10	200	6	12°·52′	β11°·18′	3·546	3·46	,,	st.	40
11	$\bar{2}1\bar{1}$	3	5°·56′	β10°·47′	3·645	..	,,	..	..
12	$22\bar{2}$	4	16°·30′	17°·52′	2·5	2·32	,,	..	14
13	$2\bar{2}\bar{2}$	5	16°·11′	17°·42′	2·53	..	w.	..	..

Note.—v.st.=very strong, st.=strong, med.=medium intensity, w.=weak and v.w.=very weak; F′=structure factor.

of the latter and the intensities of the corresponding static reflections given by Sir William Bragg (1921) and Robertson (1933). It is clear from the data given in the above table that the intensity of the dynamic reflections from the

* The plate distance for Figs. 1 and 2 is 5·2 cm. and for Figs. 3–6 is 5·7 cm.

crystal planes is by no means proportional to the intensity of the corresponding Bragg reflection. The most intense modified spot is given by the $0\bar{1}1$ plane which has a low structure factor. The planes 110, $20\bar{1}$, $21\bar{1}$ and 200 which have the highest structure factors also give rise to modified spots with medium intensity. On the other hand, in spite of the fact that the 001 plane, according to Sir William Bragg, gives the strongest reflection and has a large structure factor, the first and second order dynamic reflections by it appear only extremely weakly. The experimental results thus clearly demonstrate that the intensity of the dynamic reflections are determined by considerations very different from those controlling the intensity of the static reflections by the same planes.

4. *Significance of the Experimental Results*

The basic idea in the quantum theory of X-ray reflection in crystals is that the frequency of the incident radiation is modulated by the monochromatic infra-red vibrations of the crystal. In an earlier paper appearing in this issue it has been shown that the frequencies lying in the region of 30–100 cm.$^{-1}$ are alone effective in the modified X-ray reflections by organic crystals. Therefore for the purpose of the present discussion, we may ignore the internal vibrations of the naphthalene molecule. Since the plane of the molecules in the crystal is nearly *normal to the* 001 *plane*, five rotations and two translations out of the nine possible lattice vibrations involve movements *parallel to the* 001 *plane*. Therefore, these vibrations do not affect the structure amplitude of the latter. As the displacements of the molecules due to the remaining two lattice vibrations normal to 001 planes are also relatively small, the dynamic reflections of the X-rays from this plane resulting from those lattice vibrations should be expected to be relatively weak. The opposite situation prevails for the planes $0\bar{1}1$, 110, $20\bar{2}$ and $21\bar{1}$. The plane of the molecule is nearly parallel to them and all the lattice vibrations make their maximum contribution to the variation of the structure amplitude. Thus, even when the static structure factor is low as for $0\bar{1}1$, the Raman reflection will be very strong. The crystal planes 200, $20\bar{1}$, 120 and $11\bar{1}$ lie between these two extremes with respect to the lattice vibrations and the dynamic reflections from them will, therefore, be of medium intensity as compared with the corresponding Bragg reflection. The experimental facts observed in the present investigation are in good agreement with these conclusions.

The observations include a wide range of crystal planes making angles between 55° and 125° with the cleavage plane. It is obvious that the almost total disappearance of the reflection from the 001 plane which gives one of the strongest Bragg reflections and the great intensity of the reflection from

the $0\bar{1}1$ plane which has a very low structure factor cannot be accounted for on the basis of the Faxén–Waller theory (Zachariasen, 1940) that the observed spots are the maxima due to the diffuse scattering of X-rays by the elastic waves in the crystal.

In conclusion I express my sincere gratitude to Sir C. V. Raman, F.R.S., N.L., for his suggestions and interest in the work.

5. *Summary*

The Raman X-ray reflections from 001, $0\bar{1}1$, 110, $11\bar{1}$, $20\bar{1}$, 200, $20\bar{2}$, 120, $2\bar{1}\bar{1}$, $22\bar{2}$ and $2\bar{2}\bar{2}$ planes of a naphthalene crystal are obtained. It is observed that the first and second orders of the dynamic reflections from 001 (cleavage) plane are extremely weak, in spite of the fact that its static structure factor is high. On the other hand, these reflections from $0\bar{1}1$ plane which has a very low structure factor, are very strong. The 110, $20\bar{1}$, $21\bar{1}$ and 200 planes which give the strongest Bragg reflections also yield the Raman spots with medium intensity. These experimental facts are readily explained in relation to the known crystal structure and the lattice vibrations of naphthalene, if we assume the basic idea in the quantum theory of X-ray reflection in crystals put forward by Raman and Nilakantan that the frequency of the incident radiation is modulated by the monochromatic infra-red vibrations of the crystal lattice. A study of the relative intensities of the dynamic reflections from the different crystal planes clearly demonstrates that the character of these reflections is determined by the geometry and amplitude of the lattice vibrations.

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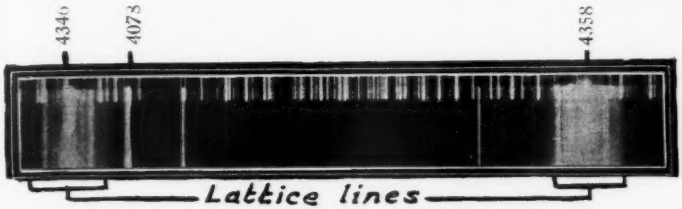

FIG. 8 Raman Spectrum of Naphthalene

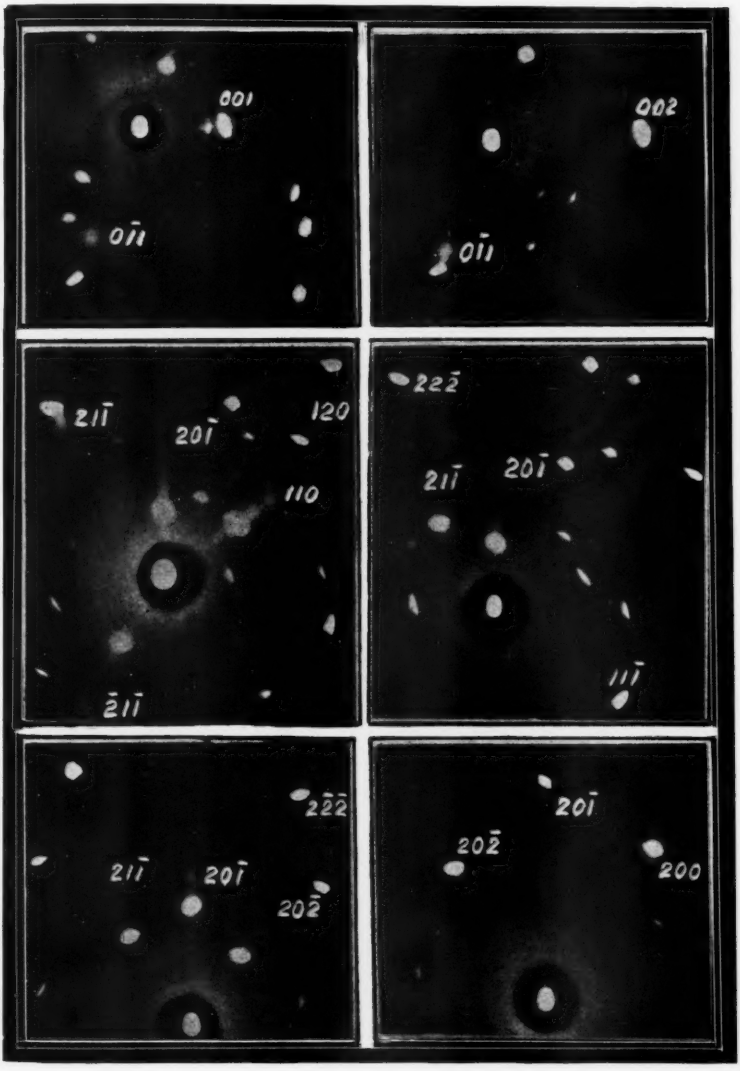

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Raman X-Ray Reflections in Naphthalene

THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: II. BENZOPHENONE

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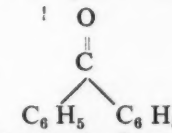
1. *Introduction*

In the first paper of this series, it was shown that the dynamic or Raman X-ray reflections from the 001 plane of naphthalene almost completely disappear as a necessary consequence of the fact that the plane of oscillating molecules in the lattice is nearly normal to this crystal plane. An exactly opposite effect is noticed in benzophenone crystal in which the intensity of the dynamic reflection is abnormally high for the 001 plane. As in the case of naphthalene, the intensity of such reflections as compared with the static ones, is also observed to depend on the orientations of the crystal and the molecular planes in the lattice.

2. *Crystal Structure and Lattice Spectrum of Benzophenone*

Benzophenone,  belongs to the ortho-rhombic bisphenoidal class (Groth[1]), having a space group D_2^4 $P2_1\,2_1\,2_1$ (Banerji and Haque[2], 1938). The dimensions of the unit cell are $a = 10{\cdot}3$, $b = 12{\cdot}11$ and $c = 8{\cdot}04$ A.U. There are four molecules in the unit cell. The X-ray analysis of the crystal structure is incomplete; but Banerji and Haque[2] have observed that most of the important crystal planes yield very strong Bragg reflections, the absent reflections being from *hoo*, *oko* and *ool* where h, k and l are odd. Krishnan, Guha and Banerji[3] (1933) have given the magnetic susceptibilities along the a, b and c axes as $\psi_a = -88 \times 10^{-6}$, $\psi_b = -88{\cdot}6 \times 10^{-6}$ and $\psi_c = -149{\cdot}3 \times 10^{-6}$ e.m.u. The refractive indices along the three directions γ, β and α (parallel to the crystal axes a, b and c respectively) are $\gamma = 1{\cdot}67$, $\beta = 1{\cdot}65$ and $\alpha = 1{\cdot}52$ (Nedungadi[4], 1941). It has been concluded from the above data of magnetic and optical anisotropies that the two benzene rings linked through the carbonyl group C = O are inclined to each other at an angle of $22°{\cdot}35'$, the plane bisecting the two

benzene rings being *normal* to the '*c*' axis. The line of intersection of the two benzene planes is inclined to the '*a*' and '*b*' axes, the angle made with the '*b*' axis being 22°·35′. Thus the biplanes of the molecule are nearly *parallel* to the 001 plane of the crystal, which is just the opposite of the condition prevailing in naphthalene.

The benzophenone molecule $(C_6H_5)_2$ CO has sixty-three possible internal vibrations. Twenty-seven of these have been observed in the Raman spectrum of the melt, of which twelve are depolarised (Nedungadi, 1941). In the crystal, in addition to these intra-molecular vibrations for each of the four molecules in the unit cell, which do not show any significant changes from the liquid, there are *twenty-four* degrees of rotational and translational freedom for the molecules, of which *twenty-one* contribute to lattice vibrations and *three* only to the Debye elastic spectrum. In the Raman spectrum of the crystal, it has been observed that the intense "wing" of the liquid on either side of the Rayleigh line is replaced by three discrete lines* at 67, 102 and 122 cm.$^{-1}$ (Venkateswaran, 1938; Gupta, 1938; and Nedungadi, 1941). It has been shown by the present author that the line at 122 has to be assigned to the deformational oscillation of the two benzene rings against each other and the other two to the lattice vibrations. Nedungadi (1941) has studied the variations of intensity of the *Raman lines* in a single crystal of benzophenone with different crystal orientations and concluded that his observations are in good agreement with the above conclusions regarding the orientation of molecules in the unit lattice.

3. The Dynamic Reflection of X-rays by Benzophenone

X-rays from a copper target are employed. A small crystal of benzo-phenone measuring approximately 2 mm. × 2 mm × 1 mm. is mounted with the 110 plane lying in a vertical plane. Three sets of Laue patterns are obtained, the first set with X-rays nearly grazing the 110 plane, the crystal being rotated about a vertical axis; the second set with X-rays incident nearly normally on the 110 plane, the crystal being rotated about a vertical axis and the third set of pictures being taken in the same way as the second set but with the crystal rotated about a horizontal axis. Figs. 2 and 3 in the accompanying Plate are the Laue patterns obtained for the first set with X-rays making glancing angles of 4°·19′ and 8°·24′ respectively with the 110 plane. Figs. 4 and 5 are the patterns for the second set, the X-rays making glancing angles of nearly 8° and 2° with $1\bar{1}0$ plane. Figs. 6 to 9 are the photographs obtained for the third set,

* See Fig. 1 in the accompanying Plate.

TABLE I

No.	Ref. to Fig.	Indices of Plane	$2\theta_i$	$\theta_i + \phi$ for Kα	Lattice Spacing in A.U.		Angle* made with 001	Intensity (Dynamic)	Intensity (Static) (Banerji)
					Exp.	Theo.			
1	6	002	12°·10′	21°·12′	4·18	4·02	0°	v.v.str.	v.str.
	7	,,	19°·54′	22°· 4′	4·02	,,	,,	,,	,,
	8	,,	29°·38′	21°·12′	4·18	,,	,,	,,	,,
2	2	$01\bar{2}$	24°·59′	22°·29′	3·94	3·82	+166°	med.	..
	6	,,	21°·12′	23°·13′	3·82	,,	+162°	str.	..
	5	012	20°·20′	22°·29′	3·94	,,	− 15°	,,	..
3	1	$10\bar{2}$	19°·28′	22°·29′	3·94	3·75	−159°	med.	..
	4	,,	21°·12′	22°·54′	3·87	,,	−160°	,,	..
4	4	$12\bar{1}$	24°· 9′	20°·47′	4·26	4·38	−160°	med.	..
5	1	022	31°·28′	27°·18′	3·26	3·35	+ 34°	med.	..
	4	,,	28°·22′	26°·59′	3·3	,,	,,	,,	..
	1	$0\bar{2}2$	22°·54′	26°·58′	,,	,,	+144°	str.	..
	2	,,	27°·21′	26°·34′	3·35	,,	+146°	,,	..
	4	,,	20°·47′	26°·58′	3·3	,,	,,	,,	..
6	1	202	22°· 3′	β 23°·19′	3·4	3·2	− 38°	str.	v.str.
	3	,,	19°·28′	26°·59′	3·3	,,	,,	,,	,,
	7	,,	22°· 4′	27°·44′	3·21	,,	− 36°	med.	,,
7	4	122	24°· 9′	28°· 8′	3·2	3·19	−41°	w.	..
8	3	$1\bar{1}1$	18°· 9′	15°·53′	5·56	5·62	45°	w.	v.str.
	5	,,	19°·28′	15°·25′	5·73	,,	,,	med.	,,
	,,	111	,,	,,	,,	,,	135°	,,	,,
9	6	132	29°·38′	32°·11′	2·76	2·75	− 48°	med.	..
	7	,,	34°·15′	32°·53′	2·72	,,	− 47°	,,	..
10	6	021	9°·47′	14°·57′	5·91	5·86	+130°	med.	..
11	2	201	17°·42′	20°·47′	4·3	4·34	− 60°	med.	..
	3	,,	22°· 4′	19°·54′	4·45	,,	− 58°	,,	..
	6	,,	15°·53′	19°·54′	,,	,,	− 69°	,,	..
12	5	131	24°·58′	26°·10′	3·4	3·41	− 65°	v.w.	..
13	1	110	8°·38′	11°·13′	7·87	7·85	90°	med.	v.str.
14	2	$2\bar{1}0$	16°·48′	18°· 9′	4·87	4·74	90°	w.	..
	3	$2\bar{1}0$	16°·47′	,,	,,	,,	,,	,,	..
15	5	$2\bar{2}0$	28°· 8′	22°· 4′	4·017	3·93	90°	v.w.	v.str.
	6	,,	26°·34′	22°·29′	3·94	,,	,,	,,	,,
16	5	130	27°·44′	23°·44′	3·74	3·76	− 90°	v.w.	v.str.
17	5	$1\bar{4}0$	28°· 8′	30°·45′	2·89	2·9	90°	v.w.	v.str.

* + sign means clockwise and − sign, anti-clockwise.

Note.—v.v.str.= very very strong, v.str.= very strong, str.= strong, med.= medium, w.= weak, v.w.= very weak.

the glancing angles made with 001 plane being nearly 0°, 6°, 10° and 15° respectively. The prominent streak appearing in all the patterns is due to the 001 plane and serves as a guide for the identification of different crystal planes giving rise to Raman reflections. In Table I the visual estimates of intensities of the dynamic and static reflections are given along with the indices of the corresponding planes, the angle they make with the 001 plane at the Bragg setting, and their lattice spacings obtained from the position of the Raman spot by making use of the formula $2\,d \sin \frac{(\theta_i + \phi)}{2} = \lambda$, and the spacing calculated from a knowledge of the crystal structure. Only the Raman spots seen in the neighbourhood of the Bragg setting are included in the table, though many of them are present in the other photographs as well.

The outstanding result of the present investigation is the enormous intensity of the dynamic reflections from the 002 plane of the crystal. The intensity of the Bragg reflection from this plane is only as much as that of several other crystal planes; but on a rough estimate its dynamic reflection is at least ten times more intense than the most prominent spot from any other plane. The data given in Table I and the photographs reproduced in Figs. 2 to 9 further show that the following planes making an angle between 0—40° on either side of 001 and $00\bar{1}$ planes also yield Raman spots with fair intensity: $01\bar{2}$, $10\bar{2}$, $12\bar{1}$, 022, $02\bar{2}$ and 202. On the other hand, the Raman reflections from the planes making an angle of nearly 90° with it, namely 110, $2\bar{2}0$, 210, $2\bar{1}0$, 130, $1\bar{4}0$ and 131, are comparatively weak. Banerji and Haque have given estimates of intensities of the Bragg reflections for only a few of the planes given in the above table. A comparison of the relative intensities of the static and dynamic reflections for these planes, however, reveals that there is no direct relationship between the intensities of both cases.

4. Significance of Experimental Results

From the above observations of the intensities of the Raman reflections from several crystal planes of benzophenone, it is clear that the intensity is a maximum when the plane is nearly parallel to the plane of the molecule and a minimum when it is nearly perpendicular to it. The results are thus analogous to those obtained for naphthalene in the earlier paper and are readily explained on the same basis as the latter. Since the unit cell of benzophenone contains four molecules, there are twenty-one possible modes of lattice oscillations ; but as the exact position and orientation of the molecules in the lattice are not known, it is not possible to analyse these

vibrations and ascertain the degeneracies involved. However, it is obvious from the known disposition of the molecules in the lattice that most of the lattice vibrations will contribute components normal to the 001 plane, thus causing a large variation of the structure amplitude of the plane. On the other hand the motions of the molecules during these vibrations being nearly parallel to the family of planes situated normal to 001 plane, their contribution to the dynamic structure factor of these planes will be a minimum. The results of the present investigation are thus in good accord with the proposed crystal structure of benzophenone.

As only three out of twenty-four degrees of rotational and translational freedom of the molecule in the unit lattice contribute to the Debye spectrum, the fraction of the total thermal energy carried by the elastic waves in the crystal is almost negligible. The diffuse scattering of X-rays by these waves should therefore be relatively very feeble, and cannot account for the great intensity of the new spots observed in the Laue photographs. Secondly, it is also evident from the habit of the crystal and its physical properties that benzophenone is much more nearly isotropic than naphthalene. This would lead us to expect the intensity of the diffuse scattering of the X-rays by the elastic vibrations by the different crystal planes to have intensities nearly in proportion to the ordinary X-ray reflections by those planes. The striking disparity actually observed in the relative intensities of the dynamic and static reflections from different planes recorded in the present investigation therefore precludes the possibility of any connection between the observed phenomena and the theory of diffuse X-ray scattering by the elastic waves in the crystal.

In conclusion the author wishes to express his respectful homage to Sir C. V. Raman, F.R.S., for his sustained interest in the work.

5. *Summary*

The dynamic reflections of X-rays from several crystal planes of benzophenone are recorded. The striking observation made in the investigation is that the intensity of the reflection from 002 plane is enormously great. Other planes on either side of the latter making angles of $0° - 40°$, also give rise to Raman spots of fair intensity. On the other hand such reflections from planes making an angle of nearly 90° with the 001 plane are comparatively weak, in spite of the fact that they give very intense Bragg reflections. These experimental results are thus in striking contrast with those obtained for naphthalene in which the dynamic reflection from the 001 plane is almost completely absent. These facts are readily

explained on the basis of the theory due to Raman and Nilakantan that they arise from the vibrations of the crystal lattice. The difference in the behaviour of these reflections for naphthalene and benzophenone is due to the fact that while in the former the plane of the molecule is normal to the 001 plane, in the latter it is parallel to the 001 plane.

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Fig. 1. Lattice Spectrum of Benzophenone

Fig. 2

Fig. 3

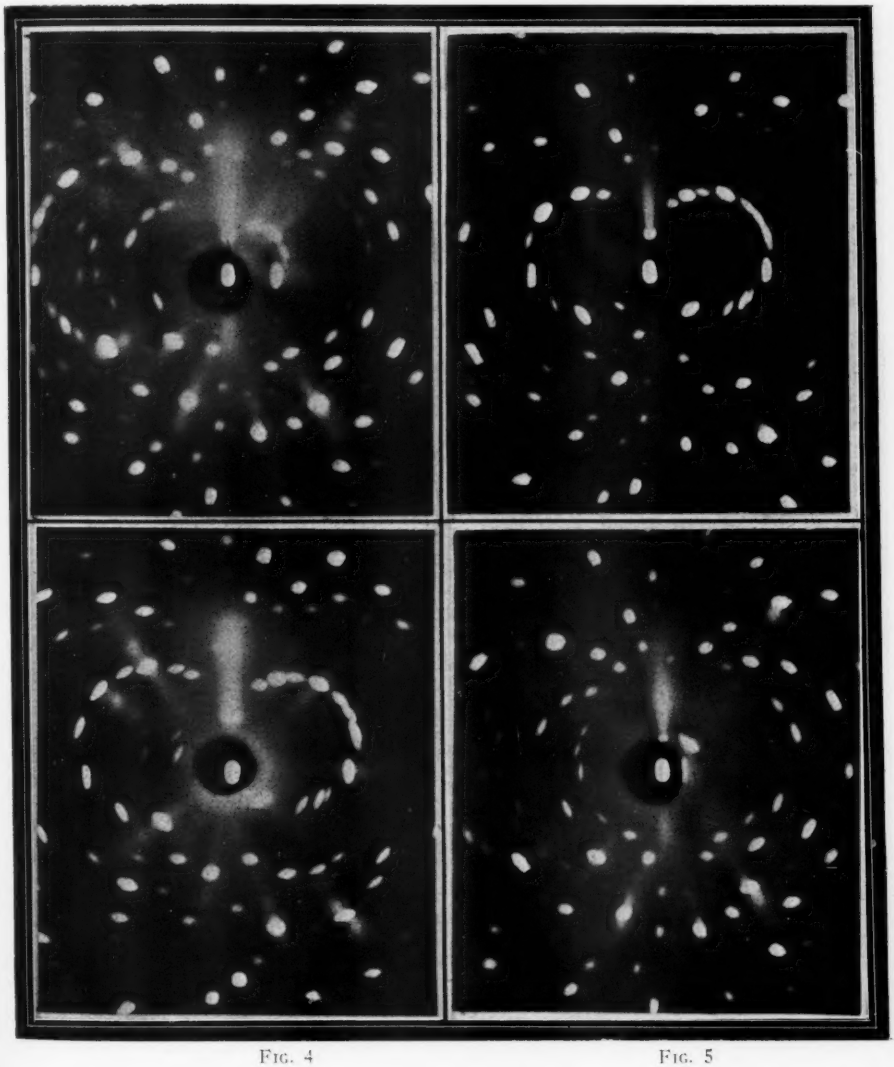

Fig. 4

Fig. 5

Raman X-Ray Reflections in Benzophenone

Fig. 6 Fig. 7

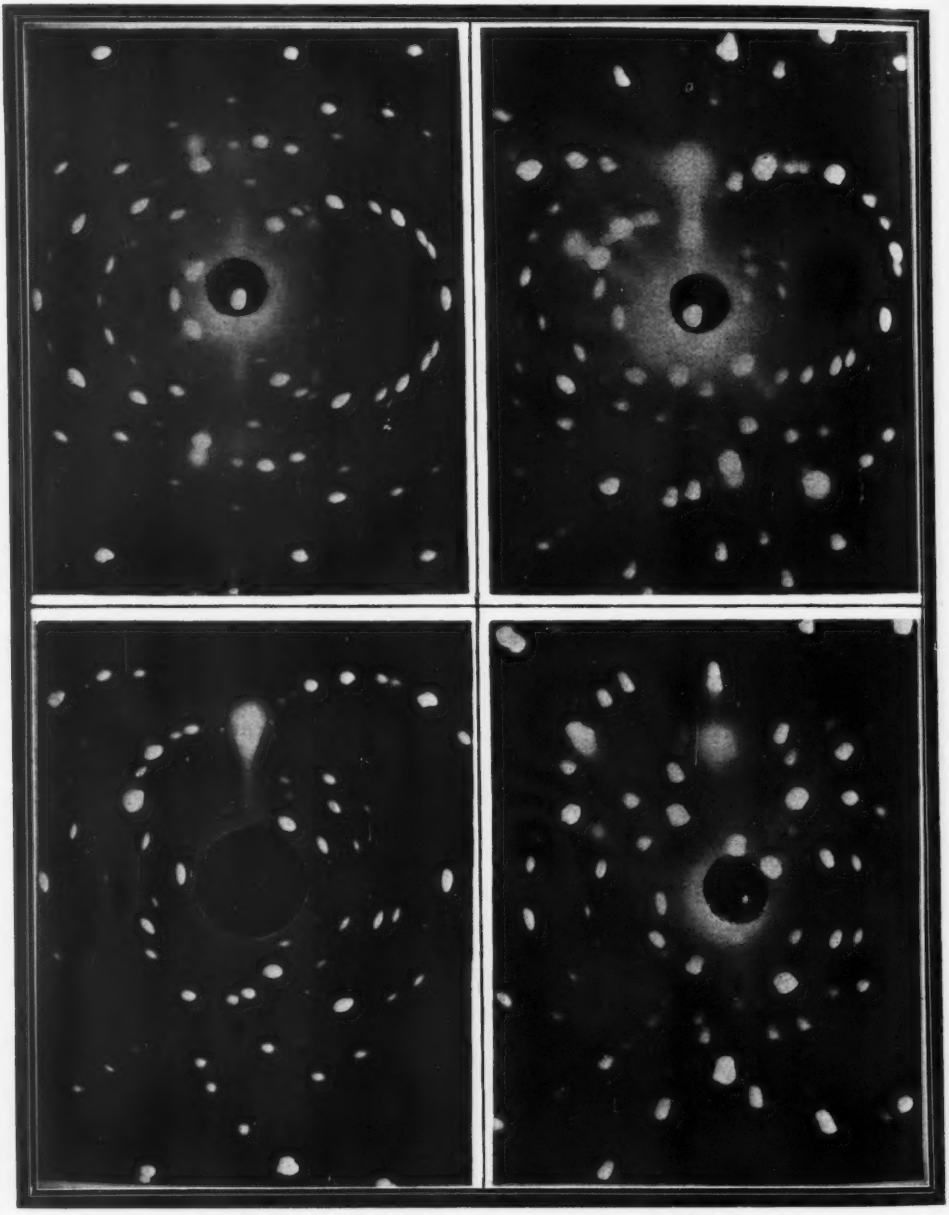

Fig. 8 Fig. 9

Raman X-Ray Reflections in Benzophenone

THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: III. HEXAMETHYL-TETRAMINE

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1. Introduction

The two earlier papers of this series dealt with crystals of aromatic compounds, *viz.*, naphthalene and benzophenone. The molecules of these crystals being highly anisotropic in shape, the effect of their translatory and rotational oscillations would be very different on crystal planes respectively parallel and perpendicular to the plane of the aromatic rings. As a result, a striking disparity in the relative intensities of the dynamic and static reflections from the different planes was observed. For the sake of comparison it is of great interest to consider the phenomena observed with hexamethyl-tetramine which is one of the few well-studied organic substances crystallising in the cubic system. On the basis of the ideas already indicated we should expect to find in this case a closer parallelism between the intensities of the Raman and Bragg reflections by the planes of the crystal. This conclusion is strikingly supported by the experimental results.

2. Crystal Structure and Lattice Spectrum of Hexamethyl-tetramine

The crystal structure of hexamethyl-tetramine—urotropin—has been investigated by Gönell and Mark (1923), and Dickinson and Raymond (1923), and with especial thoroughness by Wycoff and Corey (1934). The unit cell is a body-centred cube having an edge-length of $a = 7{\cdot}02$ A.U. and contains two molecules of $C_6H_{12}N_4$. The only planes giving first order reflections are those having two odd and one even indices.

The molecule $C_6H_{12}N_4$ possesses a symmetry T_d. Due to the high order of symmetry, many of the molecular vibrations are degenerate. There are ten modes of vibrations characteristic of the ring, of which eight are Raman active and four are infra-red active. Kohlrausch and co-workers (1938) have observed all these eight lines below 1500 cm.$^{-1}$, besides the C–H vibrations. In the crystal the two molecules of the unit cell which give in general, all the internal frequencies observed in aqueous solutions, possess

in addition twelve degrees of rotational and translatory freedom which yield the lattice and the acoustic spectra. Since the crystal has an O_h symmetry and the molecule is isotropic, it is easily seen that these will yield only one inter-molecular vibration (or hindered translation) along the diagonal of the unit cube, which is triply degenerate, and two hindered rotations which are also triply degenerate. A group-theoretical analysis of the crystal vibrations shows that the translatory vibration comes under the symmetry class F_{2u}* which is inactive in the Raman and the infra-red. One of the rotatory vibrations belongs to the class F_{1g} and is inactive in both Raman and infra-red. The other appears in the class F_{2g} and is active only in the Raman. A preliminary investigation made to record the lattice spectrum of the crystal yielded only a weak picture which indicated a faint line below 100 cm.$^{-1}$ A detailed investigation of this region with single crystals is now in progress.

3. The Dynamic Reflections of X-rays by Hexamethyl-tetramine

A tiny crystal of urotropin prepared from a solution of a mixture of water and alcohol was used in the investigation. The experimental arrangement was the same as that described in the previous communications. The X-rays were first made incident normally to the 110 plane of the crystal, which is one of its natural faces. A series of twenty-eight Laue photographs were taken with the crystal rotated about the vertical cube-edge from 0° to 45°. Figs. 1 to 8 in the accompanying Plate reproduce some of the typical photographs obtained. Fig. 1 gives the pattern when the X-rays are exactly normal to 110. The two strong dynamic reflections from 110 and $1\bar{1}0$ and four weak reflections from 011 and $0\bar{1}1$ and 101 and $10\bar{1}$ forming an irregular hexagonal pattern may be clearly observed. Besides, the four Raman spots due to (211) planes are also recorded in the neighbourhood of the corresponding Laue spots. Figs. 2 to 8 are for the positions of the crystal for which the goniometer readings are nearly 2°, 7°, 26°, 30°, 33°, 37°·30′ and 45° respectively. The only crystal planes which give Bragg reflections within the range included in the present investigation are (110), (200), (211), (220) and (222). All these reflections may be easily identified from the patterns illustrated in the Plate. Measurements of the positions of the spots were, however, made from all the twenty-eight photographs taken and the representative data are given later in Tables II to IV.

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* The notations are those used by Placzek in *Handbuch der Radiology*, Vol. 2, page 297.

4. Experimental Results and their Discussion

1. *Relative intensities of the dynamic and static reflections.*—Table I gives the estimated intensities of the Raman spots of the different planes and the intensities of the Bragg reflections given by Wycoff and Corey (W. and C.) and Gönell and Mark (G. and M.)

TABLE I

Indices of planes	Intensity (Dynamic)	Intensity (Static)	
		W. & C.	G. & M.
110	v.str.	1281	v.str.
200	med.	447	m.str.
211	str.	..	str.
220	v.w.	300	w.
222	str.	..	str.

It will be seen that the intensities of the dynamic and the static reflections are proportionate for the five planes which represent four totally different directions in the crystal. Of the three lattice vibrations of the crystal, the two hindered rotations do not change the structure amplitude of the principal planes. Hence the only vibration which is active in the Raman X-ray reflections is the hindered translation which is triply degenerate. This affects the structure amplitudes of various planes to a similar extent.†

2. *The sharpness and orientation of the Raman spots.*—One of the significant observations made on the Raman spots from the (100), (110) and (211) planes of the crystal is that they are fairly sharp and well-defined if not too far removed from the Laue reflections. This is in striking contrast to the ' diffuse ' spots that are usually recorded in crystals, *e.g.*, rock-salt or benzophenone or highly complicated structures like sorbic acid (Lonsdale, etc., 1941). This is no doubt connected with the fact that there is only one lattice oscillation which modulates the incident X-rays and the dynamic reflections in each case arise from a single set of phase-waves. When there are more than one lattice vibration involved, the observed Raman spot is the result of the superposition of a series of reflections from several phase-waves which make different angles with each other. This is presumably one of the reasons why most of the organic and inorganic crystals yield only diffuse spots at angles even slightly different from the Bragg setting.

† Theoretical calculation shows that the (100) and (111) reflections which do not appear in the Bragg are weakly active in the Raman X-Ray effect.

It may further be noticed from the illustrations that for oblique incidence, the orientation of the Raman spots is different from the corresponding Laue spots. Pisharoty (1941) has shown in a recent paper that while the Laue spots are elliptical, the Raman spots are round in shape as a consequence of the fact that the total deviation of the ray from the incident beam remains nearly constant for small changes in the angle of incidence. When the cross-section of the incident X-ray beam is not circular, but elongated as in the present investigation, the Raman spots should for the same reason, have the same shape as the direct spot and be parallel to its length. This is what is observed in the case of spots from (110) and (211) planes. It may also be observed from Figs. 2 and 6 that as the static reflection by (211) planes recedes away from the dynamic reflection, the latter deviates slightly from the line joining the central and the Laue spots. This indicates that the phase-wave responsible for the (211) dynamic reflection is not normal but inclined to the plane containing the incident beam and the normal to the crystal plane.

3. *The geometry of the dynamic reflections.*—Tables II to IV give the lattice spacing d calculated for the different planes at different crystal orientations by making use of the Raman-Nath formula (1940),

$$2\,d \sin \frac{\theta+\phi}{2} \sin\left(\vartheta + \frac{\phi-\theta}{2}\right) = \lambda \sin \vartheta,$$

where θ is the galncing angle of incidence and $(\theta+\phi)$, the angle made by the spot-maximum with the central ray and ϑ, the inclination of the phase-waves to the crystal planes. It may be seen that in the case of (200) and (110) planes, the spacing d remains nearly constant and equal to the theoretical value over a wide range of angles, if we take $\vartheta = 90°$. When the

TABLE II

(200) *Reflections*: *Phase Wave-angle* $\vartheta = 90°$. *Crystal Spacing* $= 3{\cdot}501$ Å

No.	X-ray Wave-length	2θ	$\theta+\phi$	$\phi-\theta$	Calculated Spacing in Å
1	CuK_α	15°·52′	25°·12′	9°·20′	3·455
2	,,	19°·27′	,,	5°·45′	3·448
3	,,	23°·48′	,,	1°·24′	3·443
4	,,	30°·53′	25°·26′	− 5°·27′	3·415
5	,,	34°·50′	,,	− 9°·24′	3·426
6	,,	36°·42′	,,	−11°·16′	3·429

TABLE III

(110) *Reflections*: *Phase-wave Angle* $\vartheta = 90°$. *Crystal Spacing* = 4·964 Å

No.	X-ray Wave-length	2θ	$\theta + \phi$	$\phi - \theta$	Calculated Spacing in Å
1	CuK_α and CuK_β	0°	16°·40′	16°·40′	5·102
2	,,	7°·49′	16°·54′	9°· 5′	4·995
3	CuK_α	11°· 6′	17°·25′	6°·19′	5·089
4	,,	12°·42′	17°·40′	4°·58′	5·023
5	,,	13°·30′	17°·55′	4°·25′	4·940
6	,,	16°·54′	17°·40′	0°·46′	5·007
7	,,	20°·26′	17°·55′	− 2°·31′	4·940
8	,,	24°·17′	17°·40′	− 6°·37′	5·014
9	,,	28°·20′	17°·50′	−10°·30′	4·942
10	,,	29°·12′	17°·55′	−11°·17′	4·96

TABLE IV

(211) *Reflections*: X-*Ray Wave-length* = 1·537 *A.U. Crystal Spacing* = 2·865Å

No.	2θ	$\theta + \phi$	$\phi - \theta$	Calculated Spacing in Å	
				$\vartheta = 90°$	$\vartheta = 65°·54′$
1	26°·34′	30°·53′	4°·19′	2·889	2·84
2	29°·12′	31°· 5′	1°·53′	2·876	2·83
3	31°·18′	31°·42′	0°·14′	2·886	2·885
4	31°·42′	31°·42′	0°	2·887	2·887
5	34°· 6′	31°·42′	−2°·34′	2·815	2·924
6	36°·42′	31°·54′	−5°· 0′	2·799	2·855
7	38°·48′	32°· 6′	−6°·42′	2·784	2·860
8	40°·47′	32°· 6′	−8°·41′	2·787	2·885

glancing angle is less than the Bragg angle, the apparent shift of the Raman spot due to K_β reflections merging with those of K_α is taken into account in making the calculations. This shows that the phase-waves for the lattice vibration considered are perpendicular to the (100) and (110) planes. On the other hand, for the prismatic plane (211) which makes an angle of

$65° \cdot 54'$ with 010 plane, the lattice spacing calculated using $\vartheta = 90°$ shows a progressive diminution as the angle of incidence is increased. It remains fairly constant if we put $\vartheta = 65° \cdot 54'$, as is only to be expected from the above-mentioned direction for the phase-waves. The lateral shift of the (211) Raman spot from the line joining the central and the Laue spots is also evidently connected with the azimuthal inclination of the phase-wave. The observations of the reflections from the (111) planes are neither sufficiently extensive nor sufficiently accurate to draw any conclusion regarding the phase-wave angle for those planes.

In conclusion the author desires to thank Sir C. V. Raman for his kind interest in the work.

Summary

The X-ray reflections from the (110), (200), (211) and (111) planes of hexamethyl-tetramine shows that the intensities of the dynamic reflections follow the same order as the intensities of the corresponding static reflections. The Raman spots of the crystal are relatively sharp compared to those from organic and inorganic crystals of complicated structure. These observations are readily explained by the fact that the molecular and the crystal structures of the substance have a high order of symmetry and that for the principal planes there is only one Raman X-ray active lattice vibration which corresponds to a movement of the two molecules against each other along the cube diagonal. The geometry and orientation of the spots are also found to depend on the direction of the phase-waves connected with the above vibration.

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Fig. 1 Fig. 2

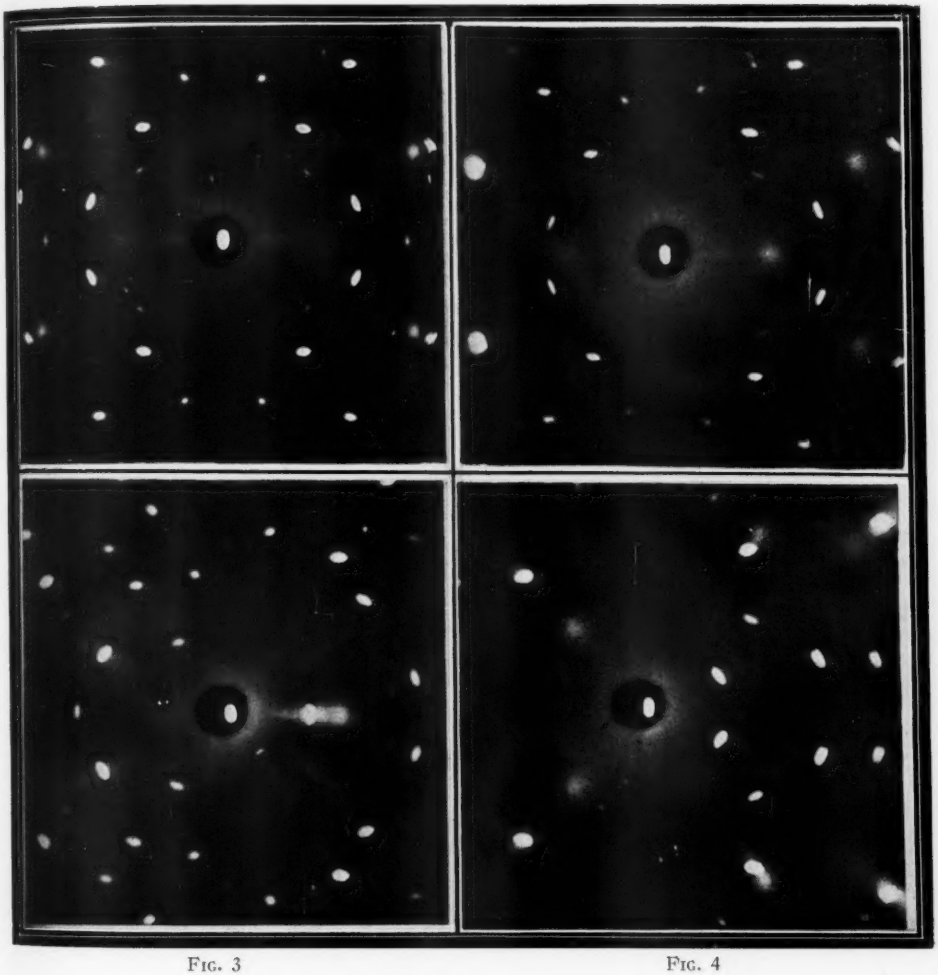

Fig. 3 Fig. 4

Raman X-Ray Reflections in Urotropin

Fig. 5 Fig. 6

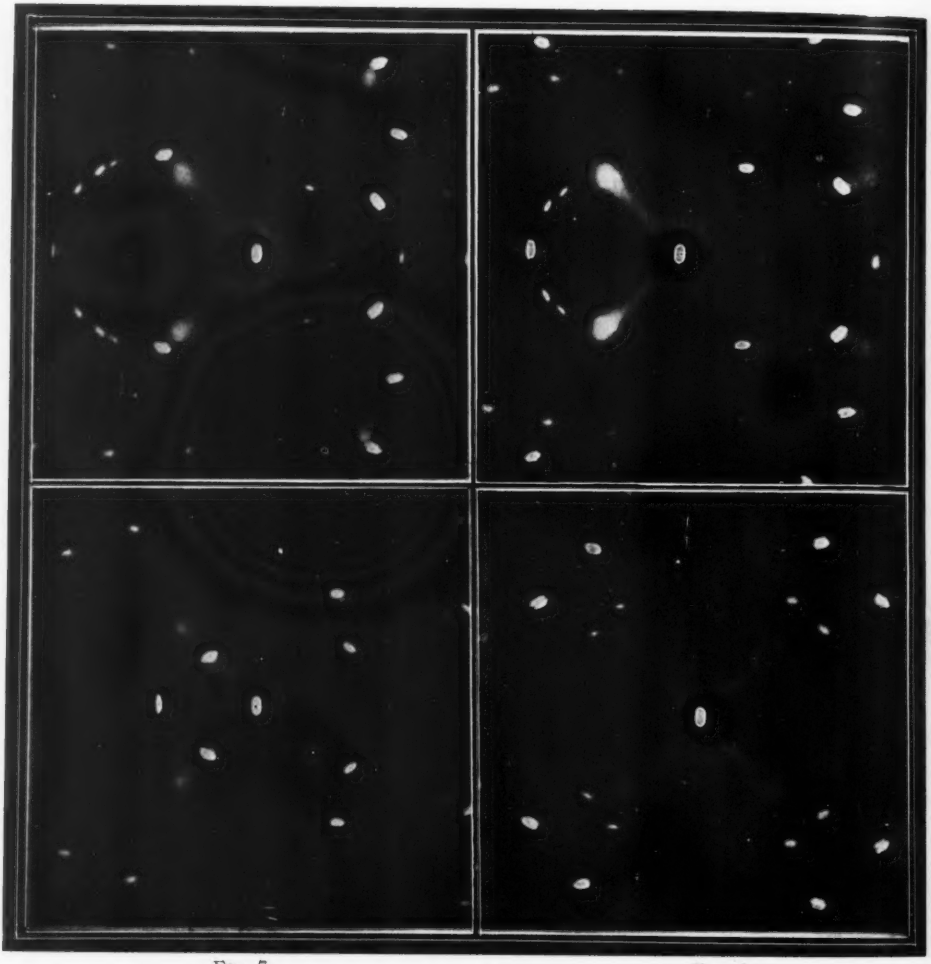

Fig. 7 Fig 8

Raman X-Ray Reflections in Urotropin

X-RAY REFLECTIONS OF THE SECOND KIND IN METALLIC CRYSTALS

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1. Introduction

The nature of the metallic state is a problem of great theoretical and practical importance. The elementary nature of metals and the simplicity of their internal structure as revealed by X-ray studies entitle them to the first place in any general discussion on the solid state of matter. It is not surprising therefore that in the earliest discussions of one of the most important problems of the solid state—the nature of the thermal energy in crystals—the exponents of the various theories namely Einstein, Debye, and Born-K'arman, looked to the data obtained with metals for experimental support. About 36 of the metals crystallize in the cubic system; fifteen of them belong to the body-centred class, while eighteen of the rest have a face-centred close-packed structure which is geometrically one of the simplest arrangements of packing a large number of spheres in the densest possible manner. Because of this structural simplicity it was for a long time supposed that Debye's theory could be applied to all the metals of the above class without reserve, and that their vibrational spectrum could be replaced by that of an elastic continuum of which the upper limit was finite and so chosen as to make the total number of degrees of freedom also finite. The earliest work by Nernst and his school did appear to support this idea, but more accurate later determinations brought out numerous cases in which Debye's theory does not fit with the experimental results; while there are some so-called anamolous cases where Debye's theory completely breaks down. In two papers appearing in the November 1941 issue of these *Proceedings*, the author has examined these points in detail and has shown that all these difficulties of the specific heat theory find a very simple explanation in the fact that the vibrational spectrum of metallic lattices includes a number of discrete monochromatic frequencies which contribute Einstein terms to the specific heat formula. In the case of a face-centred cubic lattice, for example, the unit cube consists of four atoms

having twelve degrees of freedom. The three translations of the cell as a whole contribute terms of the Debye-type, while the remaining nine degrees of freedom are assigned to the Einstein frequencies which will in general be three triply degenerate ones.

Independent evidence for the presence of discrete monochromatic frequencies in solids can be obtained by the study of the new type of X-ray reflection discovered by Raman and Nilakantan (1940) in diamond and other crystals. They have shown that the incident X-ray quantum excites the infra-red monochromatic frequencies of the crystal lattice and thereby produces dynamic stratifications of electron density. The incident quantum is then reflected by these dynamic stratifications. The geometric direction of the resulting X-ray reflection is given by the forumla of Raman and Nath (1940).

$$2\,d \sin \frac{\phi + \theta}{2} \sin \left(\vartheta + \frac{\phi - \theta}{2} \right) = n \lambda \sin \vartheta$$

where ϕ is the glancing angle of the Raman reflection, and θ the glancing angle of incidence with respect to the static crystallographic planes, while ϑ is the angle which the phase-waves make with the same static planes. It has been pointed out by these authors that the elastic waves of the Debye-type and the discrete Einstein vibrations would behave differently towards the incident quantum. The former would give rise to a general diffuse scattering with no pronounced maxima, while the latter would produce a distinct type of X-ray reflection. A study of the Raman reflection from single crystals of metals is therefore of great interest in providing a completely independent proof of the discrete frequencies in the vibrational spectrum of metals the presence of which is so strongly suggested by the specific heat considerations. From the temperature variation of the intensity of these reflections, it should be possible to evaluate the characteristic infra-red frequencies of metals as has actually been done by Dr. C. S. Venkateswaran for non-metallic crystals, as shown in an earlier paper in the present issue of these *Proceedings*.

In the present paper the author has investigated the Raman reflections from a number of planes of single crystals of aluminium for the various settings of the crystal. Some extra spots were observed by Preston (1939) in the Laue pictures of single crystals of this metal when the X-rays passed through a few standard directions in the crystal. He definitely discounted any idea of associating these spots with any lattice plane and ascribed them to diffraction by some limited groups of atoms. This idea however, is not acceptable (Born, 1941), and calculations with Preston's intensity formula

do not give the change in intensity which is actually observed when the orientation of the crystal is varied.

2. *Experimental Arrangements and Results*

Single crystals of aluminium were prepared from a wire of pure metal about 1 mm. in diameter by the stretch-anneal method (Carpenter and Elam, 1921). The orientation of the [110] direction in the crystals so prepared was generally found to be nearly parallel to the length of the wire. A Shearer-tube working at about 55 to 60 K.V. was used. The (200) Raman reflections were studied by using a molybdenum target and the other planes with a target made of silver. The period of exposure varied from 5 to 9 hours. On account of the ease with which the various planes could be studied by a simple rotation of the crystal about the goniometer axis, the crystal was so mounted that the [100] was nearly vertical. The orientation of the crystal was then adjusted in such a way that the Laue spot due to any desired plane was obtained very near the Bragg setting of the same plane for the monochromatic radiation of the material of the target. As should be expected, the Raman reflection for that plane is then observed by the side of the Laue spot. The new reflections were then photographed for various settings of the crystal about this position. The plate distance was measured separately for each position of the crystal by measuring its lateral shift in the field of view of a microscope as the crystal was rotated.

The results of measurement are given in the following tables. θ is the glancing angle of incidence, and ϕ the glancing angle of emergence with reference to the crystallographic plane given at the top of each table. 2ψ is the angle which the emergent ray makes with the incident ray while d is the spacing calculated from the Raman–Nath formula (given earlier in this paper) with the assumption that the angle $\vartheta = 90°$.

TABLE I

(200) *Raman reflections from single crystals of Al for Mo* K_α
Theoretical $d = 2{\cdot}023$ A $\vartheta = 90°$

θ	2ϕ	ϕ	$\theta - \phi$	d (Angstroms)
12°–28′	20°– 3′	7°–35′	4°–53′	2·04
11°–32′	20°–10′	8°–38′	2°–54′	2·03
11°–17′	20°– 6′	8°–49′	2°–28′	2·04
10°–21′	20°–13′	9°–52′	29′	2·02
8°–28′	20°–10′	11°–42′	−(3°–14′)	2·01
6°–52′	19°–54′	13°– 2′	−(6°–10′)	2·06
5°–32′	20°– 9′	14°–37′	−(9°– 5′)	2·04

TABLE II

(111) *Raman reflections for Ag K_α from single crystals of Al*
Theoretical $d = 2{\cdot}336$ A $\vartheta = 90°$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
4°–43′	13°–36′	8°–53′	−(4°–10′)	2·37
6°–32′ }		not separated from Laue spot		
7°–31′ }				
9°– 6′	13°–43′	4°–37′	4°–29′	2·34
9°–13′	13°–33′	4°–20′	4°–53′	2·37
10°– 2′	13°–41′	3°–39′	6°–23′	2·35
10°–33′	13°–33′	3°– 0′	7°–33′	2·38
10°–55′	13°–38′	2°–43′	8°–12′	2·37
11°–31′	13°–46′	2°–15′	9°–16′	2·34
12°– 6′	13°–38′	1°–32′	11°–34′	2·37
12°–50′	13°–38′	0°–48′	12°– 2′	2·37

TABLE III

(220) *Raman reflections for Ag K_α from single crystals of Al*
Theoretical $d = 1{\cdot}43$ A $\vartheta = 90°$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
6°–40′	22°–31′	15°–51′	−(9°–11′)	1·44
8°–59′	22°–24′	13°–25′	−(4°–26′)	1·44
12°– 4′		not separated from Laue spot		
12°–18′	22°–36′	10°–18′	2°– 0′	1·43
13°–23′	22°–32′	9°– 9′	4°–13′	1·43
15°–24′	22°–47′	7°–23′	8°– 1′	1·42

TABLE IV

(222) *Raman reflections from single crystals of Al for Ag K_α*
Theoretical $d = 1{\cdot}168$ A $\vartheta = 90°$

θ	2ψ	ϕ	$\theta - \phi$	d (Angstroms)
11°–31′	27°–31′	16°– 8′	4°–37′	1·18
12°–32′	27°–31′	14°–59′	2°–17′	1·18

3. Discussion

The spacings calculated from the Raman-Nath formula for $\vartheta = 90°$ agree very well with the known crystal spacings given at the top of each table. The accuracy of the present measurements is limited for two main reasons. In the first place in order to avoid the large absorption of the Cu K_α radiations, shorter wave-lengths had to be used; secondly the continuous radiation present gave rise to streaks which made the exact determination of the position of the Raman spot slightly difficult, particularly in positions when its separation from Laue spots was the largest. Nevertheless it can be stated that the angle between the crystallographic planes

studied and the phase-waves probably did not differ by more than ten degrees from the value ($\vartheta = 90°$) given above. This is shown by the fact that if we calculate the spacings by putting $\vartheta = 80°$, the largest difference between the spacings so calculated and those given in the column 5 of the above tables is about 2% in the case of (111) and (220) reflections and about 1% in the case of 200 ones.

The most remarkable feature about these reflections is that they are fairly sharp and not so diffuse as would be the case if they were due to diffuse scattering. The essential difference between them and the Laue spots seems to be that the boundary of the former is not quite as sharp as in the latter. The angular width of the new spots does not change very much with their position relative to the Laue spots, and appears to be largely governed by the size of the pin hole used in the camera.

The above facts seem to leave no doubt that we are dealing with a regular reflection and not with any diffuse scattering. Brindley and Ridley (1938) have given the atomic structure factors of the various planes of aluminium in the following order (of decreasing magnitude) 111, 200, 220 and 222. The same order of intensity appears with the new reflections.

In conclusion the author wishes to express his thanks to Sir C. V. Raman, KT., F.R.S., N.L., for the interest he has taken in the work and to Dr. P. Nilakantan for help in the experimental work.

4. Summary

The presence of discrete Einstein frequencies in metals which is suggested by the observed deviations from the Debye specific heat formula finds support in the fact that the various lattice planes of aluminium show strong Raman reflections. The (200), (111), (220) and (222) Raman reflections from single crystals of aluminium have been studied for a large number of settings of the crystal. It has been shown that the position, sharpness and the angular width of the new spots point to their being a new type of reflection and not diffuse maxima of X-ray scattering. The positions of the spots indicate that the angle between the crystallographic planes and the phase waves does not differ very much from 90°.

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THE LATTICE SPECTRUM AND THE RAMAN X-RAY REFLECTIONS BY ROCK-SALT

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1. *Introduction*

It has been shown in an earlier paper that the diffuse maxima observed by several authors in the Laue patterns of rock-salt are due mainly to the dynamic X-ray reflections by the monochromatic crystal vibrations as was originally explained by Raman and Nilakantan[1] (1940). In the present paper it is proposed to give an analysis of the lattice vibrations of the sodium chloride crystal and ascertain their part in determining the intensity and the geometric law of the Raman X-ray reflections from its principal planes.

2. *Group Theory and the Lattice Spectrum of Rocksalt*

The unit cube of the rock-salt lattice contains four sodium and four chlorine atoms, each group possessing tetrahedral symmetry. The co-ordinates of the atoms are

Na: $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$.

Cl: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; 0, 0, \frac{1}{2}$.

There are twenty-four degrees of freedom for the atoms in the unit cell. The crystal vibrations may be classified among the different symmetry classes of the space group O_h to which the crystal belongs, according to the following character table. The notations employed are the same as those given by Placzek[2] and the procedure followed in drawing up the table is the same as that given by Bhagavantam and Venkatarayudu[3] (1939). It will be seen from Table I that there are altogether eight modes of vibrations for the crystal all of which are triply degenerate. One of these in class F_{2u} corresponds to the translations of the unit as a whole along the three axes and may, for the present, be assigned to the Debye elastic spectrum.

Of the remaining seven, two belonging to the class F_{1u} are active in infra-red and inactive in Raman, and five in class F_{2u} are inactive in both. One of the former class corresponds to the oscillation of the sodium lattice against the chlorine lattice, and is referred to in the following as inter-lattice vibration. The remaining one of this class and one of F_{2u} correspond to the

TABLE I
Character Table for Rock-salt

O_h	E	$8C_3$	$3C_2$	6σ	$6S_4$	i	$8S_3$	3σ	$6C_2$	$6C_4$	n_j	Raman	Infra-red
A_{1g}	1	1	1	1	1	1	1	1	1	1	0		
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	0		
E_g	2	−1	2	0	0	2	−1	2	0	0	0		
F_{1g}	3	0	−1	−1	1	3	0	−1	−1	1	0		
F_{2g}	3	0	−1	1	−1	3	0	−1	1	−1	0		
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	0		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	0		
E_u	2	−1	2	0	0	−2	1	−2	0	0	0		
F_{1u}	3	0	−1	−1	1	−3	0	1	1	−1	2	f	Active
F_{2u}	3	0	−1	1	−1	−3	0	1	−1	1	6	f	Inactive
u_R	8	2	8	4	4	8	0	8	4	4			
ψ_j	24	0	−8	4	−4	−24	0	8	−4	4			
$h_j\psi_j$	24	0	−24	24	−24	−24	0	24	−24	24			

'breathing' oscillations of sodium and chlorine atoms in the unit, in one of which all the atoms move in the same phase (symmetric), and in the other the movements of the sodium and the chlorine atoms are opposite in phase (anti-symmetric). The author will go more fully into the vibrational spectrum of the crystal in a subsequent paper.

3. *The Dynamic Reflections of X-rays by Rock-salt*

The displacements of the atoms in the inter-lattice vibration are normal to the (100) planes and those of the 'breathing' oscillations are normal to the (111) planes. As a first approximation, we consider the effect of these three modes of vibrations on the intensities of Raman X-ray reflections. The other modes of vibrations would contribute only relatively feeble components normal to (100), (111) and (110) planes. If a and b are the amplitudes of the Na and Cl atoms in the direction of vibration, the co-ordinates of the eight atoms for the three vibrations are

1. *for the anti-symmetric*

$$\text{Na}: \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}; \frac{1}{2} - \frac{a}{\sqrt{3}}, \frac{1}{2} - \frac{a}{\sqrt{3}}, \frac{a}{\sqrt{3}}; \text{ etc.}$$

$$\text{Cl}: \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} + \frac{b}{\sqrt{3}}, \frac{1}{2} + \frac{b}{\sqrt{3}}; \frac{1}{2} + \frac{b}{\sqrt{3}}, -\frac{b}{\sqrt{3}}, -\frac{b}{\sqrt{3}} \text{ etc.}$$

2. *for the symmetric*

Na: Same as for 1.

$$\text{Cl}: \frac{1}{2}-\frac{b}{\sqrt{3}}, \frac{1}{2}-\frac{b}{\sqrt{3}}, \frac{1}{2}-\frac{b}{\sqrt{3}}; \frac{1}{2}-\frac{b}{\sqrt{3}}, \frac{b}{\sqrt{3}}, \frac{b}{\sqrt{3}} \text{ etc.,}$$

and 3. *for the interlattice, considering its triple degeneracy*

Na: a', a', a'; $\frac{1}{2}+a', \frac{1}{2}+a', a'$; etc.

Cl: $\frac{1}{2}-b', \frac{1}{2}-b', \frac{1}{2}-b'$; $\frac{1}{2}-b', -b', -b'$ etc.

Sir C. V. Raman has given the following expressions for the intensities of static (I_B) and dynamic (I_R) X-ray reflections at or very near the Bragg setting. For an imperfect crystal,

$$\sqrt{I_B} = \Sigma_p J_0(\zeta_p) f_p' \cos(2\pi \nu t - z_p) \qquad \text{I}$$

$$\sqrt{I_R} = \Sigma_p J_1(\zeta_p) f_p' \sin[2\pi(\nu \pm \nu^*) t - z_p] \qquad \text{II}$$

where $\zeta_p = \frac{2\pi \xi_p}{d}$, ξ_p being the component of the displacement of the pth atom normal to the crystal plane considered and d its lattice spacing. For an infra-red vibration of frequency ν^*, the amplitude a_p is given by $\Sigma_p \frac{1}{2} m_p a_p^2 = \frac{h}{4\pi^2 \nu^*}$ where m_p is the mass of the atom. The dynamic structure amplitude of any plane is then given by

$$|F|^2 = [\Sigma_p J_1(\zeta_p) f_p' \cos 2\pi N (hx_p + ky_p + lz_p)]^2 + [\Sigma_p J_1(\zeta_p) f_p' \sin 2\pi N (hx_p + ky_p + lz_p)]^2 \qquad \text{III}$$

where h, k, l are the Miller indices of the plane, N is the order of reflection and x_p, y_p and z_p are the co-ordinates of the *displaced* atom. These expressions for the 1st and 2nd order reflections by the 111, 100 and 110 planes have been deduced for the three modes of vibrations. And assuming that the frequencies of these vibrations are all in the neighbourhood of 160 cm.$^{-1}$ and remembering that they are triply degenerate, the amplitude a_p is calculated for the three cases and hence the corresponding ξ_p, ζ_p, $J_0(\zeta_p)$ and $J_1(\zeta_p)$ for Na and Cl atoms separately in each case. Substituting these values in the expressions for intensities, we get the following table for the intensities of the static and dynamic reflections.

The data given in Table II lead to the following conclusions: (1) The intensities of the dynamic reflections from (222), (200) and (220) planes are proportional to the corresponding Bragg intensities. (2) The (100) and (110) dynamic reflections should appear weakly whereas their static reflections are forbidden. The dynamic structure amplitude of (100) reflections is sufficiently

TABLE II

Intensities of Raman and Bragg X-ray Reflections

Mode of Vibration	Intensities $\lvert F \rvert^2$	Miller Indices of Planes					
		111	222	100	200	110	220
Anti-Symmetric	Raman	·11	17·7	·003	43·8	9×10^{-5}	27·6
	Bragg	310	2700	0	6624	0	4020
Symmetric	Raman	·11	17·7	·045	43·8	9×10^{-5}	27·6
	Bragg	310	2700	0	6624	0	4020
Inter-Lattice	Raman	·21	5·5	0	14·2	0	8·6
	Bragg	310	2700	0	6600	0	4000
	Raman (Total)	·43	40·9	·0453	101·8	18×10^{-5}	63·8
	$\frac{\text{Raman}}{\text{Bragg}}$	$\frac{1}{720}$	$\frac{1}{66}$		$\frac{1}{66}$		$\frac{1}{63}$

high (about 5×10^{-2}) to record the spot in well-exposed pictures. (3) The intensity of the (111) dynamic reflections is only 1/720 of the static reflections, while that of (222) is 1/66. As the Bragg intensities of (111) to (222) reflections are in the ratio 3 : 11, the corresponding ratio for the Raman intensities is 1 : 40.

4. Experimental Results

Figs. 1–4 in the accompanying Plate are four photographs taken with a crystal of rock-salt set with one of the (111) planes normal to X-rays and then rotated about [110] axis. Fig. 1 shows the trigonal symmetry, when the X-rays are nearly normal to the plane and the glancing angle on (111) planes measured from their Laue spots is 19°·36′. Figs. 2–4 are taken with X-rays making glancing angles of 11°·32′, 4°·46′ and nearly 2°·30′ with the 111 plane. On account of the great thickness of the crystal traversed by X-rays due to oblique incidence, the absorption is great and it was observed that the effective X-ray wave-length maximum is 0·46 Å. The corresponding Bragg angle for the first order of (111) reflection is 3°·40′ and for the second order is 7°·37′. The strong Raman spot of the (222) reflections may be seen in all pictures. On the other hand, the (111) Raman spot appears very weakly only in Fig. 4 in which it is very near the Bragg setting. In Fig. 3, the (111) reflection is nearer to the Laue spot than the (222) reflection and yet it is not recorded while the latter comes out with great intensity. The investigation thus clearly shows that the first order of the dynamic reflection by the (111) plane is

extremely weak which is in qualitative agreement with the theoretical calculations. These results again demonstrate that the new spots in rock-salt do not owe their origin to the scattering of X-rays by the elastic waves, for which the relative intensities of the first and second order maxima should be nearly* of the same order as of the Bragg Reflections, *viz.*, 3 : 11. The (222) Raman spots show also a drift towards the Laue spot as the crystal is rotated.

5. Phase-waves and the Geometric Law of the Raman X-ray Reflections

It may be reasonably assumed that the phase waves associated with the lattice vibrations of rock-salt will be parallel to the planes containing only either sodium atoms or chlorine atoms. Secondly the phase-waves responsible for the Raman spot lying approximately on the line joining the central and the Laue spots, should be one having the minimum azimuthal angle. From these two considerations it is assumed that the phase-waves will be parallel to the {311} planes. There are altogether twenty-four planes belonging to this "form". The geometric law of the dynamic reflections is given by Raman and Nath[5] (1940) as $2\,d \sin\frac{\theta+\phi}{2} \sin\left(\vartheta - \frac{\phi-\theta}{2}\right) = \lambda \sin\vartheta$, where d is the lattice spacing, θ is the glancing angle of incidence, $\theta+\phi$, the angle between the incident and reflected rays, ϑ is the angle made by the reflecting plane with one of the {311} planes.

Jauncey and Baltzer[6] (1941) have shown by an elegant experimental method that the diffuse maxima of the (400) and (620) planes drift towards the Laue spot as the crystal is rotated. In order to verify their data, the author has reinvestigated the case of rock-salt with Mo radiations, using a fine aperture lead-slit and a thin crystal and taking care in setting the crystal so that the plate distance remains constant for all crystal orientations. It was observed that the dynamic reflections for the 200, 400, 220 and 440 planes for Mo K_α do not show any measureable drift from the Bragg position, as is only to be expected from the above formula. Since no shift has been noticed the measurements are not given here. The extrapolated data furnished by Zachariasen[7] (1941) from a re-measurement of the reproduced photographs of Raman and Nilakantan (1940) are thus unjustifiable and are indeed contradicted by his own rigorous formula given later (Zachariasen[7], 1941).

In Tables III–V, the results of Jauncey and Baltzer[6] are given along with those of the present author. The readings in the neighbourhood of the Bragg

* According to Zachariasen's rigorous formula[4] (1941) the intensity varies as $1/\cos^2\theta_B$ for small values of $\theta_i - \theta_B$. This gives an increase of only 1·4% for the second order reflection over the first order.

angle are omitted. The phase-wave angle, *i.e.*, the angle made by the reflecting plane with one of the {311} planes, in each case is shown in the beginning of each table.

TABLE III

$\vartheta = 72°\cdot27' = 100 \wedge 113$

(400) reflections: d=2·81A Jauncey: CuK_α				(600) reflections: d=2·81 Å Author: MoK_α			
2θ	$\theta+\phi$	$\phi-\theta$	d	2θ	$\theta+\phi$	$\phi-\theta$	d
80°·14′	68°·38′	−11 ·36′	2·831	39°·12′	44°·14′	5°· 2′	2·8
78°·14′	68°·38′	−9°·36′	2·810	46°·12′	44°·31′	−1°·41′	2·82
76°·14′	68°·20′	−7°·54′	2·805	50°· 8′	45°	−5°· 8′	2·82
74°·14′	67°·50′	−6°·24′	2·809	54°·20′	45°·24′	−8°·56′	2·83
72°·14′	67°·32′	−4°·42′	2·803				
60°·14′	65°· 2′	+4°·48′	2·825				
58°·14′	64°·26′	+6°·12′	2·840				
56°·14′	64°·26′	+8°·12′	2·830				

TABLE IV

$\vartheta = 55°\cdot6' = 311 \wedge 130$

(620) reflections: d=·89 Å

Jauncey: CuK_α				Author: MoK_α			
2θ	$\theta+\phi$	$\phi-\theta$	d	2θ	$\theta+\phi$	$\phi-\theta$	d
126°·8′	123°·54′	−3°·14′	·889	43°·51′	46°·28′	2°·37′	·884
125°·8′	122°·36′	−2°·32′	·890	50°·45′	47°·21′	−3°·24′	·900
113°·8′	115°·36′	2°·28′	·894	52°·46′	47°·41′	−5°· 5′	·904
111°·8′	114°·54′	3°·46′	·891				
109°·8′	114°	4°·52′	·890				

TABLE V

$\vartheta = 82°\cdot15' = 13\bar{1} \wedge 201$, *X-ray wave-length* ·708 Å

(402) reflections: Lattice Spacing=1·26 Å

2θ	$\theta + \phi$	$\phi - \theta$	d
25°·58′	32°·17′	6°·19′	1·267
35°·24′	32°·33′	− 2°·59′	1·272
41°·24′	32°·49′	− 8°·35′	1·275
45°·46′	33°· 5′	−12°·41′	1·271
47°·30′	33°· 5′	−14°·25′	1·276
49°·50′	33°·20′	−16°·20′	1·273

Considering the limitations for accurate experimental measurements, Tables III, IV and V show that the lattice spacing obtained in every case is fairly constant and nearly equal to the theoretical value. It may be remarked here that as has been indicated by some authors, the geometric law for the new reflections is more or less similar whether they are considered as arising from the infra-red vibrations (Raman), elastic waves (Faxén-Waller-Zachariasen), or mosaic blocks (Preston-Bragg[8]). As such, any agreement between the theoretical and experimental values (see also Zachariasen[9], 1941) cannot be regarded as being in favour of one or other of these theories. Indeed, the present study shows that the geometric behaviour of the Raman reflection gives us a valuable method of determining the direction of the phase-waves in the crystal.

6. *Origin of the Streamers in the Rock-salt Patterns*

The Laue photographs of rock-salt reproduced by Raman and Nilakantan (1940) show that many of the quantum reflections have faint streamers running in different directions associated with them. These are also clearly seen in the pattern obtained by Gregg and Gingrich (1940) using monochromatic radiations, an original print of which kindly sent by them to Sir C. V. Raman was placed at the disposal of the author. These streamers have obviously a similar origin to those recorded by Raman and Nilakantan (1940) for diamond and explained in a complete fashion by Pisharoty (1941) on the assumption that associated with each of the (111) planes there are three phase waves parallel to the (100) planes. In the case of rock-salt the (311) planes take the place of the (100) planes of diamond. Calculations made on the lines indicated by Pisharoty for diamond and taking three (311) phase-waves symmetricaly situated with respect to the reflecting plane shows that the angle between streamers connected with (220) and (402) planes lies betwen 80° and 85°. Observations made on the photograph furnished by Dr. Gingrich are in

FIG. 1 FIG. 2

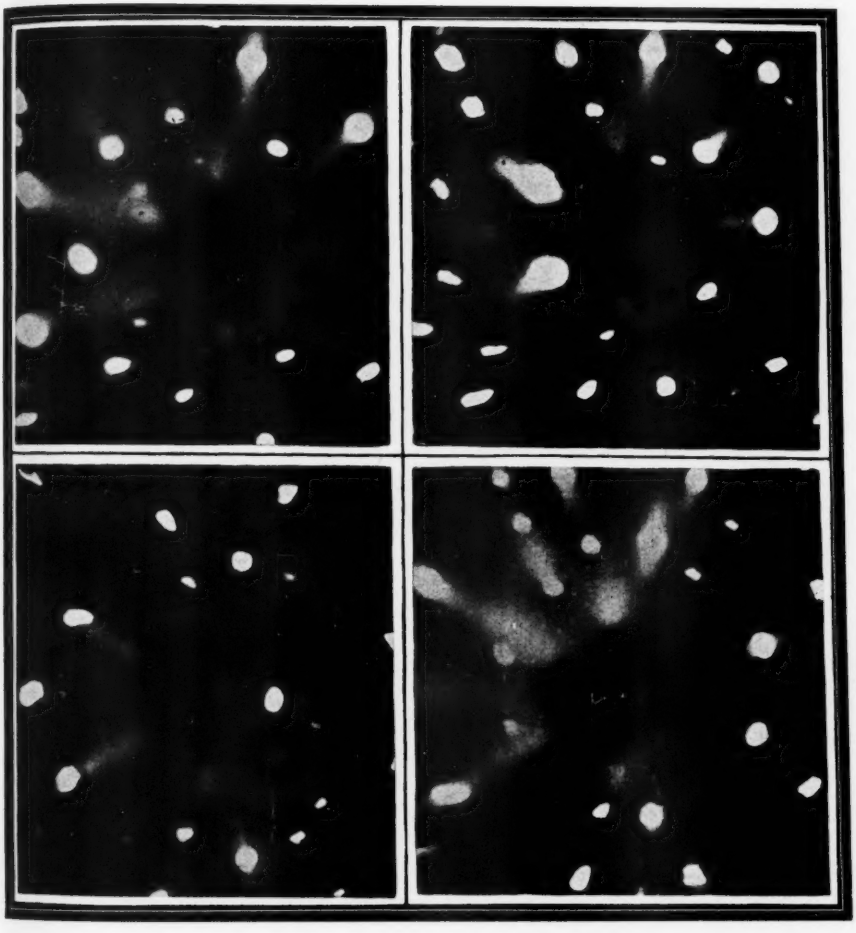

FIG. 3 FIG. 4

Raman X-Ray Reflections in Rock-salt

agreement with this calculation. It is also possible that the cross-streamers connecting the ' maxima ' are due to the combined effect of different phase-waves and require further careful consideration. A faint spot corresponding to 100 reflection is also discernible in the latter photograph and if substantiated by observations on the original negative would confirm the theoretical expectation made earlier in the paper.

In conclusion I take this opportunity to thank Sir C. V. Raman, F.R.S., for his continued interest in my work. The author's thanks are also due to Mr. Rama Pisharoty for some discussions he had with him in the calculation of intensities.

7. *Summary*

The lattice vibrations of rock-salt are analysed and the intensities of the first and the second orders of the Raman X-ray reflections from the (111), (100) and (110) planes are calculated for the three principal modes of vibration. These calculations show that the intensities of the (222), (200) and (220) Raman reflections are proportional to those of their corresponding Bragg reflections. The intensity of the (111) Raman reflection is only 1/40 of that due to (222) whereas the ratio of the corresponding Bragg reflections is 9/33. This is in agreement with experimental observations with rock-salt. The (100) and (110) Raman reflections should be very weak. The drift of the Raman spot observed by Jauncey and Baltzer for 400 and 620 and also by the present author for 600, 620 and 420 planes for different crystal orientations is satisfactorily explained on the assumption that the phase-waves are parallel to {311} planes of the crystal. The ' streamers ' that are observed in association with the ' maxima ' in rock-salt are also explained on the basis of the co-existence of at least three such waves effectively connected with any particular plane.

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THE ABSOLUTE INTENSITY OF THE RAMAN X-RAY REFLECTIONS IN DIAMOND

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1. Introduction

In an earlier paper appearing in this issue of the *Proceedings*, the author has shown how the dynamic structure amplitude of any lattice spacing of diamond may be calculated for the 1332 cm.$^{-1}$ oscillation.† The Planck oscillator of this frequency ν^* is taken to consist of two atoms and the amplitude of the oscillation is calculated by giving an energy $h\nu^*$ to each oscillator. All the oscillators are assumed to be in phase, so that we get the structure amplitude of the Raman or quantum reflection at the correct Bragg setting only. We add the *periodic* displacements of the various atoms of the unit cell to their static co-ordinates and substitute the vectorial sums, for the respective co-ordinates x_p, y_p, z_p, of the pth atom of the unit-cell, in the following expression for the structure amplitude of the reflection from the (hkl) plane:

$$F_{hkl} = \sum_p f_p \, e^{2\pi i (h x_p + k y_p + l z_p)} \, e^{2\pi i \nu t}.$$

Here f_p is the atomic scattering factor of the pth atom and ν is the frequency of the incident X-radiation. The (hkl) plane would be active for the Raman

Table I

Indices of the plane	Spacing in A.U.	Classical or Bragg reflection	Quantum or Raman reflection	Indices of the plane	Spacing in A.U.	Classical or Bragg reflection	Quantum or Raman reflection
111	2·058	A	A	400	0·889	A	F
311	1·073	A	A	420	0·795	F	A
331	0·817	A	A	422	0·726	A	F
333	0·685	A	A	440	0·629	A	F
335	0·542	A	A	620	0·562	A	F
551	0·498	A	A	622	0·537	F	A
..	..	..	..	660	0·419	A	F
200	1·778	F	A	662	0·409	F	A
220	1·258	A	F	844	0·363	A	F
222	1·029	F	A				

A—Allowed. F—Forbidden.

† Recently Nayar has found that there are discrete lattice frequencies for diamond as low as 127 cm.$^{-1}$ They are not discussed here since their modes of oscillation are not as yet known. It is possible that some of them may be active where the quantum reflections for the 1332 oscillation is forbidden. These quantum reflections if any, would be then more temperature-sensitive.

reflection whenever there is a term with frequency $(\nu \pm \nu^*)$ in the reflected radiation. The above table gives the active planes for the quantum reflection produced by the lattice oscillation of 1332 cm.$^{-1}$ The first series of planes have all their indices *odd* and every one of them is allowed for the Raman reflections. When all the indices are *even*, the Raman reflections are 'forbidden' if $h+k+l=4n$, and are 'allowed' if $h+k+l=4n+2$, the Bragg reflection being 'forbidden' for the latter case. A face-centred cubic lattice has planes in common with the diamond lattice which are 'forbidden' for the classical reflections. All of them are 'forbidden' for the quantum reflections as well.

The author has calculated in his previous paper already mentioned, that the intensity of the Raman reflection for the (111) planes of diamond in the correct Bragg setting would be about 7% of the total reflected intensity. The experiments of Raman and Nilakantan[1] showed that the intensity of the quantum reflection is fairly large when close to the Bragg setting, and that it falls off rapidly as the setting is continuously altered. But they have given no quantitative data and have not approached very close to the Bragg setting. The present paper gives an account of an experimental determination of the absolute intensity of the quantum reflections from the (111) planes, in terms of the intensity of the direct monochromatic beam.

2. *Experiments and Results*

Copper X-radiations generated in a Siefert tube of the demountable type, worked at 56 k.v. peak and 22 ma., was passed through a lead slit 0·2 mm. wide, 4 mm. high, and 130 mm. deep. The emergent narrow pencil was monochromatised by reflection at the octahedral cleavage face of a thin plate of diamond ($10 \times 6 \times 0{\cdot}8$ mm.^{3}) set at the Bragg angle of the K_α radiation. The reflected beam was easily visible on a fluorescent screen, held beyond a second slit 0·2 mm. wide and 2 mm. high, cut in a sheet of lead, and placed at a distance of 2 cm. from the crystal.

The monochromatic beam, coming through the second slit, passed through a second crystal of diamond (0·8 mm. thick), set with its octahedral cleavage face nearly normal to the incident beam. A rod of 10 cm. length attached to the goniometer of this crystal enabled it to be turned through small angles. A plane mirror attached to the goniometer was used together with a scale and telescope to measure small angular displacements of the crystal. A millimetre shift on the scale corresponded to a shift of the crystal through 1·3 minutes of arc.

After a series of trials, the second crystal was set to give Bragg reflection from the interior (111) planes, as registered on a photographic film kept

normal to the direct beam and at a distance of 4·5 cm. from the crystal. The crystal was rotated through known angles from this position, and the corresponding quantum reflections were recorded. In each case the direct beam was allowed to be incident on the film all the time, but with its intensity reduced to a known fraction by the interposition of a definite number of thin standard nickel foils supplied by the firm of Adam Hilger. Each foil was 0·033 mm. thick. The number of foils were adjusted so that the direct spot and the quantum reflection recorded on the same film were of comparable intensities. Up to five foils were used in the experiments.

A density-log. intensity curve, for the Kodak "Duplitized" X-ray films used, was drawn employing the step-wedge method of Baltzer and Nafe[2], with the incident X-rays nearly monochromatised by a nickel filter 0·066 mm. thick. All the films were developed with the same stock of developer under the same conditions of time and temperature. A Moll microphotometer supplied by Kipp and Zonen was employed for the photographic density determinations.

Measurements were taken only up to thirty minutes of arc from the Bragg setting by this method. The time of exposure for this setting was ten hours. For wider settings of the crystal monochromatisation was dispensed with, as very long exposures were required. A narrower slit was employed and the beam directly passed through the second crystal. Raman reflections for half-a-degree and one degree off the Bragg setting were recorded on the same film, one below the other, and with suitable exposures to make both of them nearly of the same photographic density. Similarly, the quantum reflection when $(\theta_B - \theta) = 2°$ was compared with the one for which $(\theta_B - \theta) = 1°$. The actual intensities were compared by assuming the value of the exponential of time, in the expression for the photographic density poduced by X-rays, to be one.

The following table gives the intensities of the quantum reflections, for various settings of the crystal, as fractions of the intensity of the direct beam.

TABLE II

$2(\theta_B - \theta)$	$\frac{\text{Intensity of the Raman reflection}}{\text{Intensity of the direct beam}}$
5′·2	0·010
10′·4	0·0029
18′	0·00085
20′	0·00028
1° 2′	0·0000020
2° 0′	0·0000004
4° 0′	0·00000008

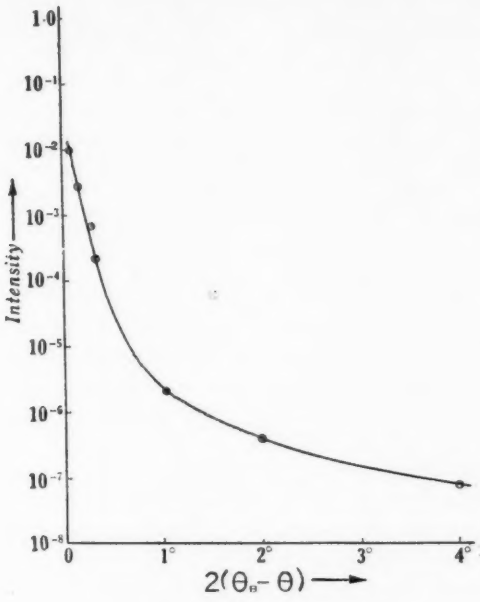

FIG. 1

Graph of Intensity against Crystal Setting

The results are plotted in Fig. 1, the ordinates being the intensities and the abscissæ being twice the difference between the Bragg angle θ_B and the glancing angle θ. It can be shown from the Raman and Nath formula[3] that,

$$2(\theta_B - \theta) \simeq 2\frac{d}{\Delta}\frac{\cos(\theta_B + \vartheta)}{\cos\theta_B}$$

where d is the crystal spacing, Δ is the phase-wave-length of the lattice oscillations, and ϑ is the inclination of the phase-waves to the lattice spacings. Hence, the curve represents the variation of the intensity of the quantum reflections with the reciprocal of the phase-wave-length of the lattice oscillations involved.

The natural divergence of the beam is determined by the width of the second slit and the far end of the first slit. This works out in the present experiment to be about four minutes of arc on either side of the central beam. To this is to be added the divergence of the Bragg reflection. But this is of the order of a few seconds of arc, for a perfect crystal of diamond, and hence negligible. Therefore there can only be some doubt about the accuracy of the first value in the above table.

3. *Discussion*

It is found that the intensity of the Raman reflection does approach a few hundredths of that of the incident beam and therefore, of the Bragg reflection itself. This is in general agreement with the theory, which indicates an intensity of about 7% of the Bragg reflection in the most favourable setting. The intensity of the quantum reflection falls with extreme rapidity at first and then more slowly with increase of the value of $(\theta_B \sim \theta)$, or from another point of view, with decrease of the operative phase-wave-length of the lattice oscillations. The facts thus suggest that, in diamond, the lattice oscillations with long phase-wave-lengths are far more probable than those with smaller phase-wave-lengths.

My sincere thanks are due to Sir C. V. Raman, F.R.S., for his invaluable help during the course of this work.

4. *Summary*

The lattice planes of diamond which are 'allowed' and 'forbidden' for the Raman reflections produced by the lattice oscillation of 1332 wave-numbers are tabulated. The intensity of the quantum reflections from the (111) planes are directly compared with the incident monochromatised X-rays, at settings ranging from a few minutes of arc to two degrees away from the Bragg setting. The results show that the intensity of the Raman reflection at the closest setting is a few hundredths of the intensities of the incident beam, in general agreement with the theoretically estimated value of 7% at the exact Bragg setting. The intensity falls off rapidly at first and then more slowly as the crystal setting is continuously altered. When the angle of incidence differs by two degrees from the Bragg value, the intensity is roughly a ten-millionth part of the incident beam.

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ON THE MULTIPLE SPOTS AND STREAMERS EXHIBITED BY THE (111) DYNAMIC REFLECTIONS IN DIAMOND

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1. Introduction

The experiments of Raman and Nilakantan[1] on the quantum reflection of X-rays from the (111) planes of diamond have definitely established that the phase-waves of the lattice oscillations, excited by the incident X-rays are parallel to the (100) planes transverse to the plane of incidence. The present paper deals with an experimental study of the effects of the other two possible sets of phase-waves parallel to the cube faces, on the Raman reflections. One of us has shown in a previous paper[2] that these sets of phase-waves also would give rise to weaker Raman reflections, in directions considerably out of the plane of incidence of the X-rays on the static spacings. In fact, the streamers and the subsidiary spots accompanying the main Raman reflection (Raman and Nilakantan, 1940) are quantum reflections arising from the dynamic stratifications produced by the combination of these waves with the static (111) spacings.

2. Experimental

A Siefert tube of the demountable type with a copper anti-cathode, run at 56 k.v. peak and 22 ma. was the source of X-rays. The horizontal X-ray beam was passed through a lead slit of the pin-hole type of effective depth 95 mm. and diameter 1 mm. The emergent pencil had a divergence of 72′. This narrow pencil was then passed through a thin triangular plate of diamond, cut nearly parallel to a set of (111) planes and held nearly nomal to the incident beam. The subsidiary phenomena accompanying the main Raman reflection were studied for angles of incidence close to the Bragg angle corresponding to the (111) planes of diamond and the Cu K_α radiation.

The crystal was set initially so that the incident plane was a plane of symmetry parallel to a (110) plane. In this position the ' streamers ' and the subsidiary spots are symmetrical about the horizontal line joining the direct spot and the Laue spot (Figs. 2*a*, *b*, *c*, Plate XXX). Other settings of the crystal were tried for which the plane of incidence was inclined to the symmetry plane. The two 'streamers' and the two subsidiary spots accompanying the main dynamic reflection are found to be dissimilar in intensity and

unsymmetric with respect to the line joining the direct spot and the Laue spot. Even the primary Raman reflection lies outside this line in these cases; but this is clearly detectable only when the reflection is sufficiently away from the Laue spot and then the subsidiary phenomena become extremely weak.

The question whether the subsidiary phenomena separate from the primary quantum reflection as the glancing angle of incidence θ, is gradually decreased from the Bragg value θ_B was studied. It was found that the region of maximum intensity along the ' streamer ' gradually shifted away from the strong Raman reflection, thereby showing that the streamer was a specular reflection very much elongated by the divergence of the beam and the obliquity of the corresponding phase vector to the surface of the sphere of reflection. However, whether there is a bridge connecting this region of maximum intensity to the main Raman reflection or not can be settled only by the use of very fine beams having the divergence of only a few minutes of arc.

3. *Explanation of the Phenomena*

The direction of the Raman reflection is found with the help of the ' sphere of reflection '. The direction of incidence is represented by OI = $1/\lambda$ and the vector IC represents the reciprocal lattice vector $1/d$. When C is

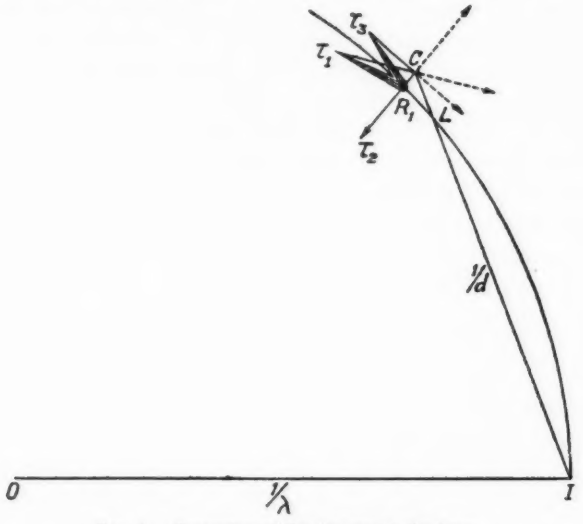

FIG. 1. Geometry of the Raman Reflections

on the sphere of reflection, the Bragg reflection is observed. No classical reflection is possible when C is either inside or outside the surface of the sphere of reflection. $C\tau_1$, $C\tau_2$ and $C\tau_3$ represent the directions of the reciprocal vectors of the phase wave-lengths of the lattice oscillations excited by

the incident X-rays, and respectively parallel to the three cube edges of the unit cell of diamond. These phase-waves combine with the static lattice spacings and give rise to dynamic stratifications which produce the Raman reflections whenever the reciprocal vectors of these resultant spacings fall on the surface of the sphere of reflection.

If the plane of incidence is a symmetry plane, $C\tau_2$ is in the plane of incidence and the Raman reflection lies in the same plane as the classical reflection. The quantum reflections caused by the two vectors $C\tau_1$ and $C\tau_3$ are symmetric with respect to this plane. When C is outside the sphere, *i.e.*, $\theta < \theta_B$, $C\tau_1$ and $C\tau_3$ make only *small* angles with the surface of the sphere of reflection and they give rise to very elongated spots, which appear as 'streamers' due to the finite *divergence* of the beam (Fig. 2*a*, Plate XXX). On the other hand when the end C of the reciprocal lattice vector is within the sphere of reflection, *i.e.*, $\theta > \theta_B$, the vectors $C\tau_1$ and $C\tau_3$ meet the sphere at larger angles and give rise to two quantum reflections, which are drawn out into two elliptic spots (Fig. 2 *c*, Plate XXX) by the divergence of the beam.

In a previous paper[2] by one of us a quantitative formula was derived for the distance of the subsidiary spot from the main Raman reflection in terms of the distance between the Laue spot and the Raman reflection, for the symmetrical setting. It is approximately

$$0{\cdot}68 \operatorname{cosec} (35°16' - \theta).$$

Actual measurements for two different settings of the crystal giving the subsidiary spots are given below:—

Plate distance = 4·35 cms.

Glancing angle of incidence	Distance between Laue spot and Raman spot	Distance between the primary Raman spot and a subsidiary spot	
		Experimental	Theoretical
22° 24′	1·2 mm.	3·5 mm.	3·7 mm.
23° 28′	2·8 mm.	7 mm.	9·3 mm.

However, when the plane of incidence is not a symmetry plane, $C\tau_2$ is not in the plane of incidence and $C\tau_1$ and $C\tau_3$ are no longer symmetric with respect to the plane of the classical or Laue reflection. Hence in both the cases $\theta > \theta_B$ and $\theta < \theta_B$, the subsidiary spots and the 'streamers' are unsymmetrical, and the difference in the lengths of the reciprocal vectors $C\tau_1$ and $C\tau_3$ give different intensities for these reflections, as actually observed. Figs. 2*d*, *e* and *f* in Plate XXX show the 'steamers' and the subsidiary spots when the plane of incidence makes 10° with the symmetry plane.

The inclination of the vectors $C\tau_1$ and $C\tau_3$ to the surface of the sphere being small (only about 13°), a rotation of the whole configuration through 10° with IC as axis would make one of these vectors leave the surface of the sphere. Hence, only one of the ' streamers ' would be left behind and this would extend both ways if the setting is the correct Bragg setting.

The existence of these triple quantum reflections suggests that the three sets of phase-waves are not capable of combination among themselves, thus showing that the lattice oscillations are incoherent when they differ in phase-wave-lengths. Otherwise, we would have phase-waves of all possible orientations thus destroying the specular character of the quantum reflections. However, the quantum reflections are distinctly separate only when the crystal setting is off the Bragg setting by the divergence of the incident beam or more. The phase-wave-length corresponding to the quantum reflection in this position is nearly 150 A.U. or less. For nearer settings, the operative phase-wave-lengths are much greater, but due to the divergence of the beam we are not in a position to settle whether the corresponding lattice oscillations are coherent or not.

The question of coherence or incoherence of the lattice oscillations of different phase-wave-lengths in the direction of the three cube-edges of diamond, was tested out experimentally in light scattering by Nayar.[3] A crystal of diamond was illumined by a narrow parallel pencil of light incident at the correct angle so that the phase-waves parallel to a cube face may reflect the light with altered frequency. The scattered light was observed spectrographically in the proper direction of reflection and in directions upto 20° on either side of it. He found that the Raman line exhibited the same intensity in all these directions. The facts about light scattering indicate therefore, that lattice oscillations of phase wave-lengths of 2000 A.U. or more are coherent and that they combine to give phase waves of all possible orientations. In the X-ray field this means a change in the glancing angle of only a few minutes of arc from the correct Bragg setting. Hence the problem of coherence in diamond of the lattice oscillations for different phase-wave-lengths can be settled only by observing the subsidiary phenomena with X-ray beams having a divergence of 5 minutes of arc or less.

4. Remarks on the Influence of Mosaic Structure in Diamond

The X-ray experiments and the spectroscopic investigations in this laboratory have all been conducted with the ordinary type of diamond. The theoretical investigations have also been carried out only for the perfect crystals. The studies of Julius, Angstrom and Reinkober[4] have shown the existence of a second variety of diamond which, unlike the ordinary variety, is transparent to the infra-red radiations in the neighbourhood of 8μ.

Robertson, Fox and Martin[5] have made extensive investigations on the various properties of this type of diamond and have come to the conclusion that it possesses a definite mosaic structure. A specimen of this type has been recently procured in this laboratory, but no X-ray studies have been conducted with it as yet. While this paper was going to press, a note in *Nature* by Lonsdale and Smith[6] has reached India where it is stated that this rare type of diamond does not exhibit the subsidiary phenomena forming the subject of the present paper, and also indicating that the ordinary or Bragg X-ray reflections given by it are stronger. It is shown below that the mosaic structure readily explains these facts.

Robertson, Fox and Martin have remarked that the second type of diamond gives a higher value for the ratio of the intensity of the (111) reflection to that of the (222) reflection than the ordinary type and have put this forward as an evidence of its mosaic structure. In a paper[7] appearing in this issue of the *Proceedings*, one of us has shown that the (222) reflections can be explained quantitatively as Raman reflections produced by the lattice oscillations of *infinite* phase-wave-length produced in the crystal. In a rotation or oscillation method, the (111) planes of a mosaic crystal would give the reflection over a greater angular range so that its intensity would be more than that for the normal type. On the other hand, the (222) quantum reflection would be much weaker as the size of the mosaic would effectively prevent the co-operation between the neighbouring parts of the crystal required for such a weak reflection to manifest itself. Hence it is not surprising that the ratio of the intensity of the (111) to the (222) reflection is large for the second type of diamond.

In another paper[8] appearing in this issue, one of us has pointed out the great rapidity with which the intensity of the Raman reflection falls off with decrease in the phase-wave-length of the lattice oscillations. It means therefore, that even for a perfect crystal the structure amplitudes for these subsidiary reflections are extremely small, so that very large numbers of regular co-operating planes are needed to produce an appreciable intensity of the subsidiary reflections. In a mosaic crystal, the lack of co-operation between different mosaic blocks would therefore reduce the intensity of the subsidiary reflection to a small fraction of the value for the perfect crystal. Hence it is but natural that the subsidiary phenomena, weak even with a perfect crystal, cease to be observable with the rarer type of diamond whose mosaic structure is an accepted fact.

Lonsdale and Smith have also observed that the Raman reflections are absent, (*a*) along the (001) axis for the (220) and (113) dynamic planes, (*b*) along the (010) axis for the (202) and (131) planes, and (*c*) along the (100) axis for the (022) and (311) planes. This fits in beautifully with the concept

of phase wave-normals along the three cube edges, in which case the observed inactive directions are exactly tangential to the surface of the sphere of reflection when the plane of incidencce is a symmetry plane. In this setting the other two phase vectors cut the sphere of reflection in the plane of incidence.

The authors wish to record their deep sense of gratitude to Sir C. V. Raman, KT., F.R.S., for his kind and helpful guidance in the course of this work.

5. *Summary*

The existence of three sets of phase waves of the lattice oscillations in diamond is shown to give rise to three quantum or Raman reflections from the (111) planes. Two of these reflections form very elongated spots which appear as streamers, due to the divergence of the beam and the obliquity of the corresponding reciprocal phase vectors, when the glancing angle of incidence θ is smaller than the Bragg angle θ_B. These reflections appear as discrete subsidiary spots when $\theta > \theta_B$. The behaviour of these reflections with respect to intensity and orientation, when the plane of incidence of the classical reflection is (1) parallel to, and (2) inclined to, a (110) symmetry plane of the crystal, is described and accounted for. The question as to the coherence of the lattice oscillations of differing phase-wave-lengths has been examined, and it is shown that all oscillations of phase-wave-lengths of the order of a thousand lattice spacings or more are coherent, while those with phase-wave-lengths of the order of a hundred lattice spacings or less are definitely incoherent. But the exact stages at which the incoherence sets in is still unsettled. The differences in the behaviour of the various planes in the normal type of diamond towards the subsidiary spots and 'streamers' and the absence of the subsidiary phenomena in the rare type, both observed by Lonsdale and Smith, have been accounted for. The larger value of the ratio of the intensity of the (111) to the (222) reflection as recorded by Robertson, Fox and Martin for the type II diamond is explained on the basis of its mosaic structure.

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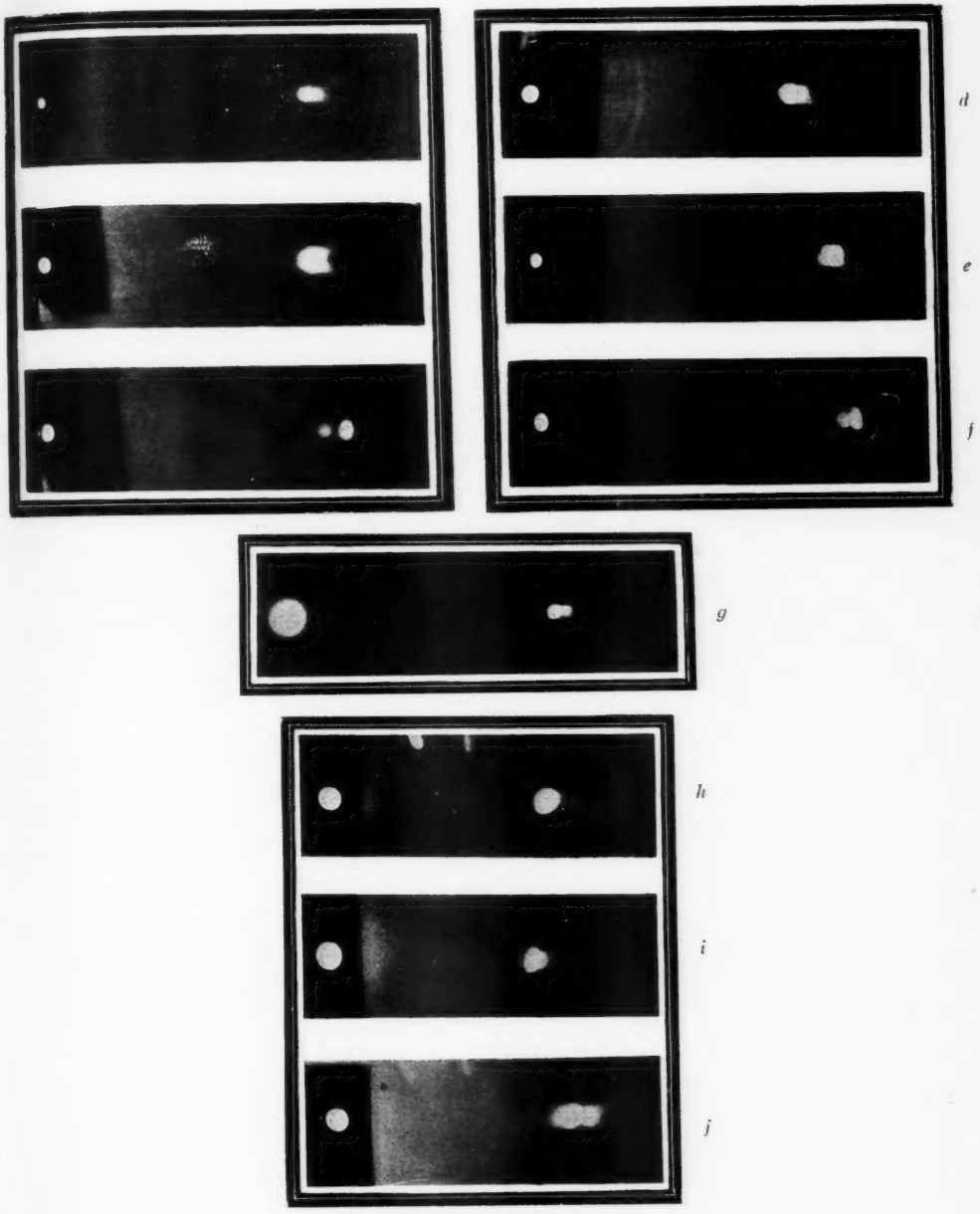

FIG. 2

Streamers and Multiple Spots observed with Diamond

ON THE RAMAN X-RAY REFLECTIONS IN ORGANIC CRYSTALS: IV. BENZIL

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

Early in the history of the study of X-ray diffraction in crystals following Laue's discovery of 1912, it was realised that the disturbing effect of the thermal agitation on the X-ray phenomena was a matter of considerable importance. About the same time, the theory of the specific heat of solids due to Debye in which the thermal energy of crystalline solids was identified with that of the elastic vibrations in them was coming into general favour. It was therefore natural that the considerations of the temperature effect in X-ray diffraction should be based on the same hypothesis. In fact, the first attempt in this direction was made by Debye himself, and the further improvements of the theory both by Debye and by later workers in the field rested on his basic concepts. Even in the specific heat theory of that time, however, it was recognised that the thermal energy of crystals which were not of the simplest chemical composition included what were called "Einstein" terms arising from modes of molecular vibration with specific frequencies. That these vibrations had any part to play in the X-ray phenomena does not however, appear to have been realised either by the experimenters or by the theorists. The great importance of the Einstein vibrations in X-ray physics, and the striking and distinctive phenomena to which they give rise, were first pointed out by Sir C. V. Raman and Dr. P. Nilakantan in their article in *Current Science* for April 1940. The study of these phenomena, in fact, has opened up a new approach to the problems of the solid state. The importance of the Einstein or characteristic frequencies of the crystal lattice is particularly evident in considering the X-ray behaviour of organic crystals. Taking for instance the case of benzil, it is known (Allen, 1927 and Banerjee and Sinha, 1937), that the hexagonal lattice of this crystal contains 3 molecules per unit cell. Even ignoring the numerous possible "internal" modes of their vibration, we have still to consider no fewer than 18 degrees of freedom of molecular movement, of which no less than 15 are necessarily represented by specific frequencies of vibration; the remaining three degrees of freedom alone of translatory movements of the lattice cell are the maximum number which can possibly be assigned to "elastic

vibrations" of the Debye type. It is thus evident that, in organic crystals, the Einstein vibrations of the lattice involving hindered rotations or translations of the molecules are of far greater importance than any possible vibrations of the elastic solid type.

In the three preceding papers of this series, Dr. C. S. Venkateswaran has considered repectively the cases of naphthalene, benzophenone and hexamethylene-tetramine. His work has proved conclusively that the situation is as described in the preceding paragraph. In the two crystals of the aromatic class dealt with by him, the very striking result emerged that the lattice planes which are parallel or nearly parallel to the planes of the aromatic rings give Raman reflections of marked intensity, while those perpendicular or nearly perpendicular to them are, by comparison, practically inactive in this respect. In fact, a striking disproportion was evident in the relative intensities of the classical and quantum reflections by the crystal planes differently situated with respect to the planes of the aromatic rings. Dr. Venkateswaran has remarked that these results find a simple explanation in the nature of the molecular oscillations which vary the structure amplitudes of the crystal planes. The hindered rotations and translations of the molecules as well as the deformational oscillations of low frequency would almost exclusively vary the structure amplitudes of the planes parallel to the aromatic rings, leaving unaffected those nearly perpendicular to them.

The fact that benzil is very similar in chemical composition to benzophenone, the former being diphenyldiketone and the latter diphenylketone, made it desirable to include this substance in the present series of investigations. It may be mentioned in this connection that a few photographs obtained with benzil were reproduced with a note in *Nature* (1940) published by four workers of the Royal Institution in London.

2. *Crystal Structure of Benzil*

Benzil belongs to the same crystal type as α-quartz, and has, in fact, an optical rotatory power stronger than that of quartz along the hexagonal axis. As already mentioned, the unit cell contains three molecules. The dimensions of the cell are $a_0 = 8{\cdot}15$ A.U. and $c_0 = 13{\cdot}46$ A. U. and the X-ray evidence indicates that the three molecules are arranged in equivalent positions within the cell about the threefold screw axis. Krishnan, Guha and Banerjee have studied the diamagnetic behaviour of the crystal and found that the gram-molecular susceptibility along the trigonal axis is $\chi^{\parallel} = -80{\cdot}0 \times 10^{6}$ e.m. units and that perpendicular to the trigonal axis is $\chi_{\perp} = -125{\cdot}6 \times 10^{6}$ e.m. units. The crystal shows a noticeable birefringence, $\omega = 1{\cdot}6588$, and $\epsilon = 1{\cdot}6783$ (Groth, *Chemische Krystallographie*) for the sodium line. Suggestions regarding the molecular structure and the molecular

orientation in benzil were made by Banerjee and Sinha (*loc. cit.*), but these conclusions have been disputed by Lonsdale and Knaggs (1939) in a brief note. No definite conclusions regarding the structure of benzil appear, however, to have been published by these latter authors.

3. *Experimental Arrangements*

Benzil is usually crystallised from ether. Due to the rapid evaporation of ether, most of the crystals are often found to be of disproportionate growth, forming a cluster. In the present work, the crystals were grown out of a solution of the substance in alcohol diluted with an equal volume of water. The smaller solubility of the substance in alcohol, assisted by the slow evaporation of the liquid facilitates a good growth of crystals suitable for X-ray work. The crystals were yellow hexagonal prismatic needles, approximately $\frac{1}{2}$ mm. in diameter. The source of X-rays was a Siefert 'Spektro-Analyt' tube of the non-demountable type, with a copper anticathode, run at 41000 volts, and 10 m.a. A fine beam of X-rays collimated by means of a lead slit 1 mm. in diameter and 9 cm. deep was incident on the crystal which was mounted on a goniometer with its trigonal axis nearly vertical. Initially one of the external prism planes of the crystal was normal to the X-ray beam, this having been judged by the optical reflection from that face. The crystal was turned through an angle of about 20° from this position about the vertical axis of the goniometer, which was adjusted to coincide with the triad axis of the crystal. The plane giving an intense Raman reflection along the horizontal was found to be the $2\bar{2}00$ plane, and a series of pictures was then taken up to a limit of about 4° on either side of this setting. In these extreme positions, exposures varying from about 2 to $2\frac{1}{2}$ hours were required.

For another series of pictures, the crystal was mounted in such a way that the X-ray beam passed along the trigonal axis. By suitable manipulation of the crystal this way or that about the goniometer axis, and aided by a number of trial pictures, the exact direction of the beam along the trigonal axis was secured. In this position, exposures varying from 2 to 3 hours were found necessary to secure a well-exposed pattern.

4. *Description of the Experimental Results*

Only two of the typical photographs obtained have been reproduced, although a number of others in different settings of the crystal have been taken. Fig. 1 *a* in Plate XXXI represents a symmetric Laue photograph with the X-rays passing along the trigonal axis of the crystal, while Fig. 1 *b* represents one with the X-rays perpendicular to the trigonal axis. Both photographs reveal some very interesting features. It will be observed from Fig. 1 *a*, that the Laue pattern exhibits hexagonal symmetry with respect to the positions of the spots. The *intensities*, however, exhibit only a trigonal

symmetry, alternate sectors showing noticeable differences in the intensity of the spots. This feature is particularly striking in the Raman pattern of six spots at the corners of a regular hexagon; the alternate spots are of the same intensity, but differ greatly from the intervening ones in this respect. Though no quantitative measurements of intensity have been made, it is fairly clear that these differences are much greater than those of the corresponding Laue spots forming a hexagonal pattern. It is also noticed that streamers emerge from the primary Raman spot, proceeding approximately parallel to the adjacent sides of the hexagon, a noteworthy feature being that these alternately point in opposite directions. The three pairs of spots showing the intense Raman reflections have been identified as belonging to the form $(2\bar{2}01)$. Lying on the same radial lines as these and forming an outer hexagon are the spots of the form $(3\bar{3}02)$ which have however much less intensity. In two of them the Raman K_α spots are just visible beyond the Laue position, two of the other spots of this group coinciding with the Bragg reflection. Here again in the neighbouring Raman spots, the intensities appear to differ.

Equally remarkable are the features seen in Fig. 1 *b*, obtained as has already been mentioned with the direction of the X-ray beam normal to the trigonal axis of the crystal. There are two groups of Laue spots lying along two ellipses. These are accompanied by two groups of Raman spots lying on vertical lines in the photograph. The group to the left of the picture is much more intense than the group to the right, while in each group, the spots differ notably in intensity among themselves; the order of relative intensities is exactly reversed on the two sides of the picture. The zone to which the more intense Raman spots belong has been identified to be the (110) zone, while the other is the $(1\bar{1}0)$ zone. On the left, the central Raman spot lying along the horizontal has the index $2\bar{2}00$, the one immediately above and below belong to the $2\bar{2}01$ planes, and the one further up that of the $2\bar{2}02$ plane. On the other zone the corresponding spots which appear belong respectively to the $\bar{2}110$, $^{-}\bar{2}111$ and $^{-}\bar{2}112$ planes. Of all the Raman spots seen, by far the most intense is that given by the $2\bar{2}01$ plane. It is thus exactly the same set of planes which give the intense reflections seen in Fig. 1 *a*.

5. *Discussion of the Results*

Bearing in mind what has been said already in the introduction, it is clear that the only possible explanation for the results indicated is that the plane of the aromatic rings in the benzil crystal lie in or very close to the alternate planes of the form $(2\bar{2}01)$. It is readily seen that this explains every one of the features indicated above. The angle between the triad axis of the crystal and the $(2\bar{2}01)$ plane is by calculation 14° 6′. It is thus evident that the plane of the aromatic rings in the crystal are inclined to the triad axis at an

(a)

(b)

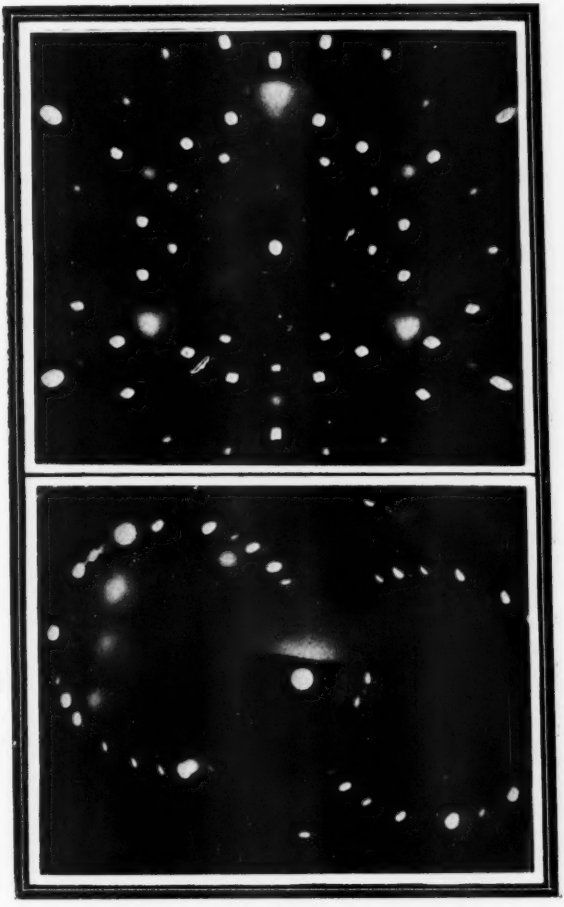

FIG. 1

Raman X-ray Reflections in Benzil

angle about the same as that stated above. The inclination of the plane of the aromatic rings thus directly inferred from the X-ray photographs, agrees closely with the angle 13° calculated by Banerjee and Sinha from the magnetic measurements of Krishnan, Guha and Banerjee. It should be remembered that the X-ray method is definitely superior to the magnetic method as it indicates both the azimuth and the orientation of the planes and not merely the latter.

The explanation of the configuration of the streamers accompanying the Raman reflections is fairly simple. By symmetry, the phase waves of the lattice must be along the three planes inclined at 120° to each other and passing through the triad axis of the crystal, these planes being perpendicular to the longer axis of the benzil molecules. The directions of the streamers as observed conform to this situation.

My sincere thanks are due to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his invaluable help and inspiring guidance throughout the course of this investigation.

6. *Summary*

In a series of well-exposed Laue diagrams of benzil taken with a pencil of Cu X-radiation along the trigonal axis, three alternate planes of the form $(2\bar{2}01)$ are found to give intense Raman reflections, the alternate planes of the same form being much less active in this respect. A similar feature is also observed in photographs taken with the beam transverse to the trigonal axis. The facts find a very simple explanation when it is assumed that the three molecules of benzil in the unit cell lying in equivalent positions along the threefold screw axis, have the planes of their aromatic rings practically coinciding with the planes mentioned. The inclination of 14° of the aromatic planes thus inferred from the X-ray results is in close agreement with the angle of 13° deduced from the diamagnetic susceptibilities of the crystal. The X-ray method is however obviously superior as it gives both the azimuth and orientation of the aromatic rings.

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QUANTUM REFLECTION OF X-RAYS IN CALCITE

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1. Introduction

Calcite is usually regarded as a crystal suitable for precision X-ray research, the intensity of the reflections given by it being much nearer those calculated for an ideal crystal than for instance in the case of rock salt. Calcite should therefore be particularly well-suited for quantitative studies of the type of X-ray reflection which involves a change of frequency and is analogous to the well-known Raman effect in crystals. A strongly exposed Laüe photograph showing numerous such reflections by the crystal planes of calcite was reproduced with a letter by Sir C. V. Raman and Dr. P. Nilakantan under date the 18th of August 1940 which was published in the issue of *Nature* dated the 19th October 1940. Attention was there drawn to the appearance in the photograph simultaneously of the quantum reflections of the first, second and third orders by the cleavage planes of calcite, as well as the well-defined character of the quantum reflections. In the present paper, some further observations on the subject are described and additional photographs are reproduced.

The explanation of the appearance of X-ray reflections with altered frequency is, broadly, that the encounter between the X-ray quantum and the crystal lattice results in the infra-red vibrations of the latter being excited, the incident quantum going off with diminished energy in a direction determined by one or other of the different sets of lattice planes in the crystal. The possibility of such a process and the experimental evidence that it actually occurs in the case of the (111) planes of diamond was indicated by Sir C. V. Raman and Dr. P. Nilakantan in an article in *Current Science* for April 1940. In view of the universality of the phenomenon and its great significance in crystal physics, it would appear desirable to present some considerations of an elementary character which may help to elucidate these new ideas.

Regarding a crystal as a pattern in space of atoms, molecules or ions grouped together in an orderly fashion, we notice that the essential feature of it is the repetitive or periodic character of such arrangement. It is this periodicity which gives us the regularly spaced layers of atoms capable of giving monochromatic X-ray reflections of the usual kind when the rays are

incident on them at an appropriate angle. The concept of a crystal as a purely static ordering of atoms is, however, untenable since such static arrangement can be disturbed in a variety of ways, in particular, by the incidence of the radiation itself, as actually happens in the Raman effect with visible light. It is necessary, in fact, to consider the various possible modes of vibration of the regular assemblage of atoms which we call a crystal. For such a vibration to possess a frequency which can be specified with perfect mathematical rigour, the disturbance should be completely periodic both in space and time, in other words, the ions, atoms or molecules should vibrate in identically the same way, with the same frequency, amplitude and phase in all the lattice cells of the crystal. During such a vibration, the crystal does not lose its character as a space-periodic grouping of the atoms, but becomes in addition a time-periodic structure. It is vibrations of this type which are characteristic of the crystalline state and which appear as sharply-defined lines in the Raman spectra.

Applying now the same electrodynamic principles as those by which Laue derived his well-known conditons for the observation of X-ray diffraction in crysals, we see that the secondary radiations from the atoms in a crystal executing monochromatic vibrations automatically divide themselves into three groups, those of the original or undisturbed primary X-ray frequency ν and two others having frequencies $\nu \pm \nu^*$, where ν^* is the frequency of the atomic vibration. Since ν^* is a strictly monochromatic frequency, the radiations from the atoms in the different lattice cells having a frequency $\nu+\nu^*$ or $\nu-\nu^*$ should be capable of interfering with each other and therefore also of giving diffraction patterns having these radiation frequencies in the same way as the radiations of unmodified frequency ν. The situation, it will be noticed, is closely analogous to that arising in the Raman effect. It should be emphasised that such X-ray reflections with altered frequency are possible only when the atoms in all the lattice cells vibrate in identically the same fashion, in other words, with vibrations having the characteristic crystal frequencies. The position is entirely different in regard to the ordinary or elastic vibrations of the lattice. These have a continuous spectrum of frequencies and merely disturb the regularity of the crystal structure. They give rise to a weak X-ray scattering which should be unobservable except when relatively large volumes of the crystal are operative. The introduction of quantum-theoretical ideas in dealing with either type of effect becomes inevitable in view of the change of frequency, exactly as in the case of the Raman effect. The alteration of frequency means an exchange of energy between the X-ray quantum and the crystal, and this can only occur in one direction or in the other, but not in both directions simultaneously. Accordingly,

we would in general have at low temperatures *only* the reflections of diminished frequency, $\nu - \nu^*$, reflections of increased frequency $\nu + \nu^*$ being however possible at higher temperatures.

2. *Crystal Structure and Lattice Spectrum of Calcite*

As is well known, calcite crystallises in the rhombohedral division of the hexagonal system. The distribution of the Ca and CO_3 ions around each other as indicated by the X-ray analysis is very similar to that of the Na and Cl ions in the rock-salt lattice. The calcite lattice may, in fact, be described as a distorted rock-salt structure, the distortion arising from the fact that the oblate CO_3 group replaces the spherically symmetrical Cl ion in it. The Ca and CO_3 ions lie alternately along lines parallel to the trigonal axis of the crystal.

The various modes of vibration with specific frequencies of which the calcite structure is capable may be divided into three groups: (*a*) internal vibrations of the CO_3 groups, (*b*) rotational oscillations of the CO_3 groups about axes respectively parallel and perpendicular to the trigonal axis and (*c*) translatory vibrations of the Ca and CO_3 ions relative to each other. So far as the X-ray problem is concerned, vibrations of the class (*a*) may be left out of consideration in view of their high frequency and relatively small effect on the structure amplitudes of the crystal planes. We are therefore principally concerned with vibrations of the classes (*b*) and (*c*). Here again, except with reference to certain special planes in the crystal, it may be assumed that the vibrations of the class (*c*), namely, movements of the Ca and CO_3 ions relative to each other are the more important, as they would influence the structure amplitudes of the lattice planes strongly. Such vibrations may be divided into two sub-classes, namely, those in which the movements of the Ca and CO_3 groups are predominately parallel to the trigonal axis, and those in which the movements are perpendicular to it. Vibrations of the first sub-class would influence the lattice planes normal or nearly normal to the trigonal axis, while those of the second sub-class would leave these unaffected. The position would be reversed with regard to crystal planes which are nearly parallel to the trigonal axis.

Raman effect investigations show that calcite has two low-frequency vibrations having wave-number shifts of 156 and 283 respectively. The latter is almost certainly a rotational oscillation of the CO_3 group about a line perpendicular to the triad axis. In the long-wave region of the infra-red spectrum, Liebisch and Rubens observed reflection maxima at 106, 330 and 357 wave-numbers, the second of these appearing only in the ordinary ray. It must be assumed that there are in addition, other modes of vibration which are inactive both in infra-red absorption or reflection and in the Raman effect.

The existing theoretical investigations of the vibrations of the calcite lattice concern themselves with the unit-cell containing two $Ca\,CO_3$ groups. It is not yet clear whether these give a really satisfactory explanation of the observed spectroscopic behaviour of calcite.

3. Specular Character of Raman Reflections

Figs. 1*a* and *b* in Plate XXXII reproduce two X-ray diffraction photographs obtained using copper K_α radiations and a needle-shaped crystal of calcite bathed by the X-ray pencil. The needle was prepared by dissolving out a cleaved rod of calcite in dilute hydrochloric acid until it was thin enough, thus avoiding all possibility of spurious effects due to distortion of the crystal or formation of disturbed surface layers. The needle is seen as a dark shadow crossing the direct X-ray beam. The Laue and the Raman reflections by the (211) planes of the crystal are seen side by side, the former in two different positions corresponding to the two different settings of the crystal, while the latter appears in the two pictures as a narrow streak in directions making nearly the same angle in both cases (14° 44′ and 14° 47′) with the direction of the incident rays. The dynamic spacing calculated from these angles is practically identical with the known static spacing of the (211) planes of calcite, namely 3·03 A.U.

Figs. 3*a*, *b*, *c* and *d* in Plate XXXIII reproduce a series of four Laue photographs obtained with a thin and perfectly flawless cleavage plate of calcite. The X-rays from a molybdenum target tube run at 45000 peak voltage and 12 milliamperes were employed, the beam emerging from a cylindrical pin-hole 93 millimetres deep and 1·6 millimetres diameter. The plate to film distance was 5 centimetres. In Fig. 3*c*, the X-ray beam was nearly normal to the cleavage face of the crystal, while in Figs. 3*b* and 3*d*, the beam made angles of 7° 14′ and 5° 16′ respectively with the normal to the surface. In Fig. 3*a*, the X-ray beam grazed a set of lattice planes within the crystal parallel to an external surface of cleavage. The photographs being well-exposed, they exhibit, besides the usual Laue reflections a great number of quantum reflections by the lattice planes of the crystal which may be readily identified from the angular positions of the spots with reference to the direct X-ray beam.

Though the Raman reflections as recorded in the photographs do not appear so sharply defined as the Laue spots, it should not be supposed that this is due primarily to any inherent diffuseness in the reflections. This is clearly indicated by Figs. 1 *a* and *b* where their linear width as recorded on the plates appears actually less than that of the more strongly exposed Laue reflections. As explained by Mr. Rama Pisharoty in the July 1941 issue of

these *Proceedings*, very striking differences in the appearance of the Laue and the Raman reflections arise as the result of several factors, namely (*a*) the finite lateral extension of the X-ray beam, its angular divergence and the variation of its intensity within the cross-section of the beam; (*b*) the difference in the nature of the reflection, *viz.*, white and monochromatic respectively, as also the difference in their relative intensities and the geometric laws which they obey, and (*c*) the finite thickness of the crystal employed. The X-ray beam employed in obtaining Laue photographs has usually a considerable angular divergence, being in the present experiments nearly 2 degrees of angle. Fig. 4 in the text illustrates the effect of the arrangement employed to restrict the divergence of the beam on the distribution of intensity inside it.

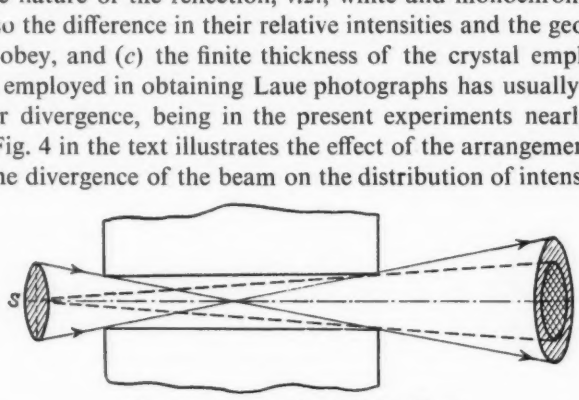

FIG. 4. Cross-Section of X-Ray Beam

It is evident from the figure that there would be an intense central part in the emerging beam having a diameter slightly larger than that of the pinhole and a less intense peripheral part; these we may designate as the umbra and penumbra respectively. The reflection of the intense central cone of rays would naturally be the first to be recorded, while the reflection of the penumbral rays would follow later. Accordingly, unless the exposures are sufficiently prolonged, a certain lack of sharpness in the boundary of the reflection is inevitable. A similar lack of definition at the edges would also result from the finite thickness of the plate, as illustrated in Fig. 5. This again would be much more obvious in recording a weak reflection photographically than a strong one.

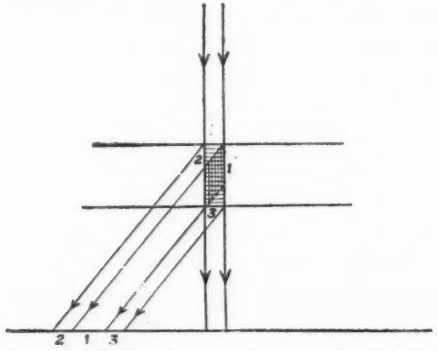

FIG. 5. Reflection from a Plate of Finite Thickness

It should not, however, be inferred from the foregoing remarks that the Raman reflections of calcite are geometrically as sharp as those of the (111) planes in diamond. Indeed, it is obvious that there is a great difference in the behaviour of various crystals in this respect. The reflections of calcite, for instance, are definitely superior in definition to those of sodium nitrate which has a very similar crystal structure. It is evident that one of the factors which make for sharpness of the reflections is the rigidity of the bindings in the crystal. This is indicated by the fact that the frequencies of the similar modes of lattice vibrations are much higher for calcite than for sodium nitrate.

4. Geometry and Intensity of Raman Reflections

As already mentioned above, the particular crystal planes which give the quantum reflections are in most cases readily identified. For this purpose, we measure the angular distance of the spots from the direction of the central beam and hence calculate the dynamic spacing responsible for the reflection; this is then compared with the known list of the static spacings of the crystal giving an appreciable intensity of reflection. The disagreements are never large. If there be any doubt, this can be resolved by analysing the Laue diagram and identifying the planes giving associated Laue reflections. A fairly complete analysis of all the Raman reflections seen in Fig. 3 *c* which refers to the case in which the crystal is set with its cleavage face normal to the X-ray beam is exhibited geometrically in Fig. 6.

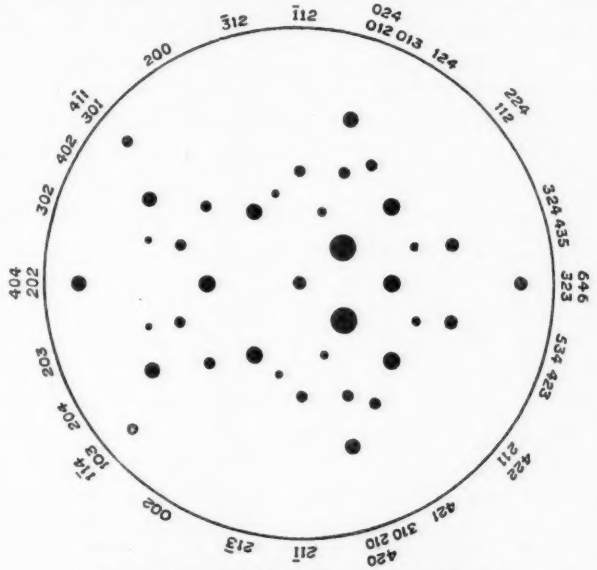

FIG. 6. Raman Reflections in Calcite Crystal

Comparing Fig. 3 *c* with Figs. 3 *b* and 3 *d*, it will be seen that though the Laue patterns themselves are completely different, the Raman reflection patterns show only changes of intensity and no noticeable changes in the position of the spots.

Table I gives a detailed list of all the crystal spacings in calcite which have been identified from the Laue photographs as giving quantum reflections. The table has been put in to emphasise the fact that numerous crystal planes give these reflections and that within the rather restricted range of

TABLE I

Raman Reflections in Calcite

Miller Indices	Glancing angle θ	Glancing angle ϕ	Dynamic spacing in A.U.	Static spacing in A.U.	Intensity estimate
112	3° 2′	10° 18′	2·99	3·03	10
	9° 52′	3° 27′	3·04	3·03	10
	14° 39′	−1° 14′	3·06	3·03	3
224	9° 52′	19° 8′	1·52	1·52	2
	14° 39′	12° 11′	1·53	1·52	6
336	18° 50′	12° 28′	1·01	1·01	4
	19° 25′	11° 53′	1·01	1·01	..
200	12° 19′	6° 53′	2·12	2·09	5
	13° 3′	6° 9′	2·12	..	5
	7° 8′	12° 8′	2·12	..	5
	6° 16′	13° 7′	2·11	..	4
400	18° 59′	20° 36′	1·05	1·045	6
	17° 29′	21° 52′	1·05	..	4
012	10° 27′	7° 24′	2·29	2·28	2
	10° 14′	6° 24′	2·32	..	2
	11° 23′	6° 45′	2·25	..	0·5
	10° 58′	7° 2′	2·27	..	..
024	16° 26′	19° 20′	1·15	1·14	4
	16° 13′	19° 57′	1·14	..	4
	17° 54′	18° 30′	1·14	..	5
	17° 50′	18° 26′	1·14	..	5
$\bar{1}12$	14° 54′	10° 18′	1·62	1·60	2
	13° 58′	11° 8′	1·63	1·60	3
	15° 17′	9° 43′	1·64	..	2
	15° 11′	10° 1′	1·62	..	2
	14° 40′	10° 38′	1·62	..	2
	15° 34′	9° 26′	1·64	..	2
323	12° 49′	8° 41′	1·90	1·91	10
	19° 3′	..	1·94	..	4
202	12° 37′	8° 41′	1·92	1·93	4
	17° 53′	..	1·97	..	..

TABLE I (*contd.*)

Miller Indices	Glancing angle θ	Glancing angle ϕ	Dynamic spacing in A.U.	Static spacing in A.U.	Intensity estimate
235	19° 34′	15° 38′	1·17	1·18	3
	19° 1′	16° 5′	1·17	..	..
556	20° 40′	19° 38′	1·02	1·03	6
	20° 50′	19° 48′	1·02	..	..
512	16° 59′	22° 43′	1·04	1·04	2·
	17° 29′	22° 7′	1·04	..	..
411	22° 54′	20° 24′	0·96	0·96	1
	23° 13′	20° 9′	0·96	..	..
446	20° 57′	18° 31′	1·05	1·06	2
	21° 26′	17° 58′	1·05	..	..
435	18° 17′	15° 25′	1·23	1·23	..
	18° 21′	15° 17′	1·23	..	4
302	12° 15′	15° 11′	1·50	1·47	..
	12° 0′	15° 32′	1·49	..	1
301	13° 58′	12° 54′	1·53	1·52	5
	14° 4′	12° 42′	1·53	..	4

settings of the crystal employed, the dynamic spacings do not diverge noticeably from the static values. Only in a few cases, however, are the settings sufficiently varied to enable any conclusions to be drawn about the value of the phase-wave inclination, ϑ, to the crystal planes under study. In the case of the (112) planes, for instance, there is a distinct progressive change of the dynamic spacing with alteration of the crystal setting, indicating that ϑ is definitely smaller than 90°. A more detailed investigation, however, would be necessary to settle this matter definitely.

A careful study of the Laue patterns shows that the Raman reflections do not always lie on the same radial line as the corresponding Laue reflections. A distinct lateral shift or azimuth effect is detectable in a number of cases. The streaks due to the white radiations are also in certain cases not radial. Only when the plane of incidence coincides with a crystallographic plane of symmetry that it can be definitely said that there is no lateral shift or azimuth effect. Usually, however, the Laue and Raman reflections are too near each other and the size of the spots too large to arrive at any definite conclusions. The fact that the azimuth effect is observable at least in certain cases indicates that the phase waves in calcite, as in diamond, have an orientation and an azimuth standing in definite relation to the crystal structure.

It may also be mentioned in passing that a careful analysis of the four Laue patterns reproduced as Fig. 3 revealed the presence of a few diffuse spots in each case whose origin could not be definitely identified.

The intensities shown in the last column of Table I are of course, only relative, and vary with the setting. They are, however, of some interest in relation to the question as to the relative intensity of the Bragg and Raman reflections by the individual planes. Theory indicates that there is not necessarily a proportionality between the static and dynamic structure amplitudes of a set of lattice planes, the latter depending on the particular modes of vibration responsible for the dynamic reflection. While broadly it may be said that the planes which give strong Bragg reflections, *e.g.*, the cleavage planes, also give strong Raman reflections, there are evidently exceptions to this rule. In particular, the (556) planes which are nearly normal to the trigonal axis of calcite give Raman reflections which are remarkably strong considering their relatively small static structure amplitude. It should be remarked in this connection that serveral of the possible lattice vibrations in calcite involve movements of the Ca and CO_3 ions along the trigonal axis, and hence should give marked variations of the structure amplitudes of planes normal to it. A fuller study of this point would obviously be of great interest.

Figs. 2*a* and *b* in Plate XXXII illustrate the effect of rising temperature on the relative intensity of the classical and quantum reflections in calcite. The two types of reflection exhibit a reciprocity of behaviour, a marked diminution of intensity in the classical reflection with rise of temperature being accompanied by a marked increase of intensity of the quantum reflections. It is noteworthy that the (210) planes of calcite do not exhibit the exceptional behaviour observed with the same planes in sodium nitrate crystals.

5. *Summary*

The paper presents the results of a preliminary study of the X-ray reflections of the second kind observed in calcite. Numerous planes in this crystal exhibit such reflections, the dynamic spacings in most cases varying but little with the setting of the crystal. Observations are recorded concerning the sharpness of the reflections, their intensity and the influence of temperature on the same. The results are considered in the light of the quantum theory of X-ray reflection.

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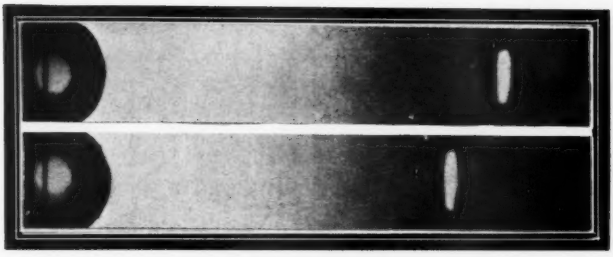
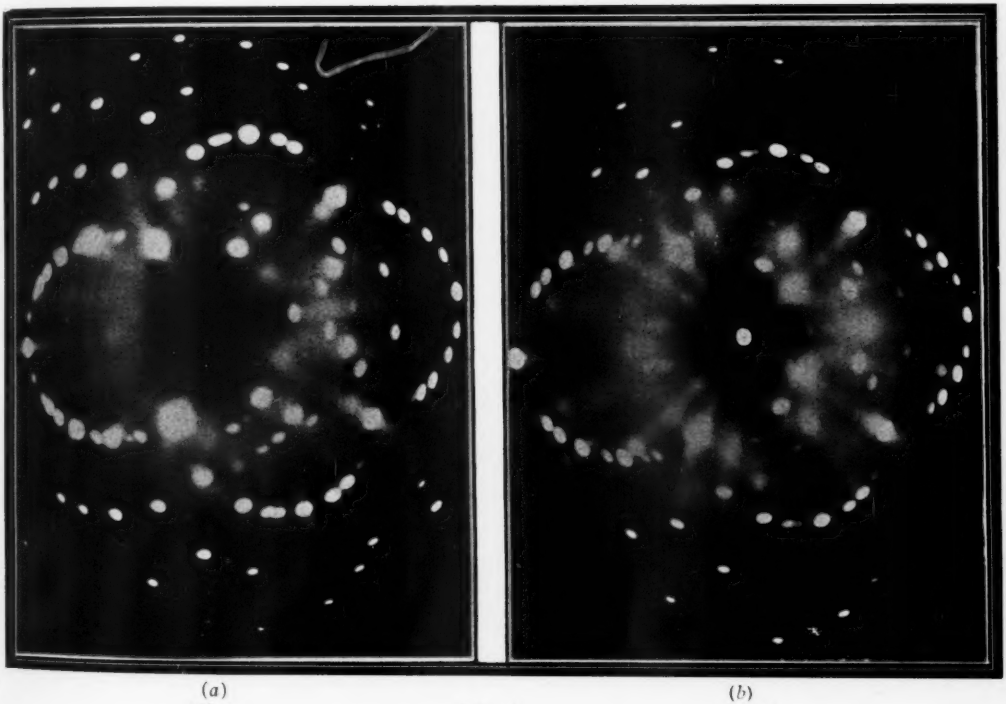


FIG. 1

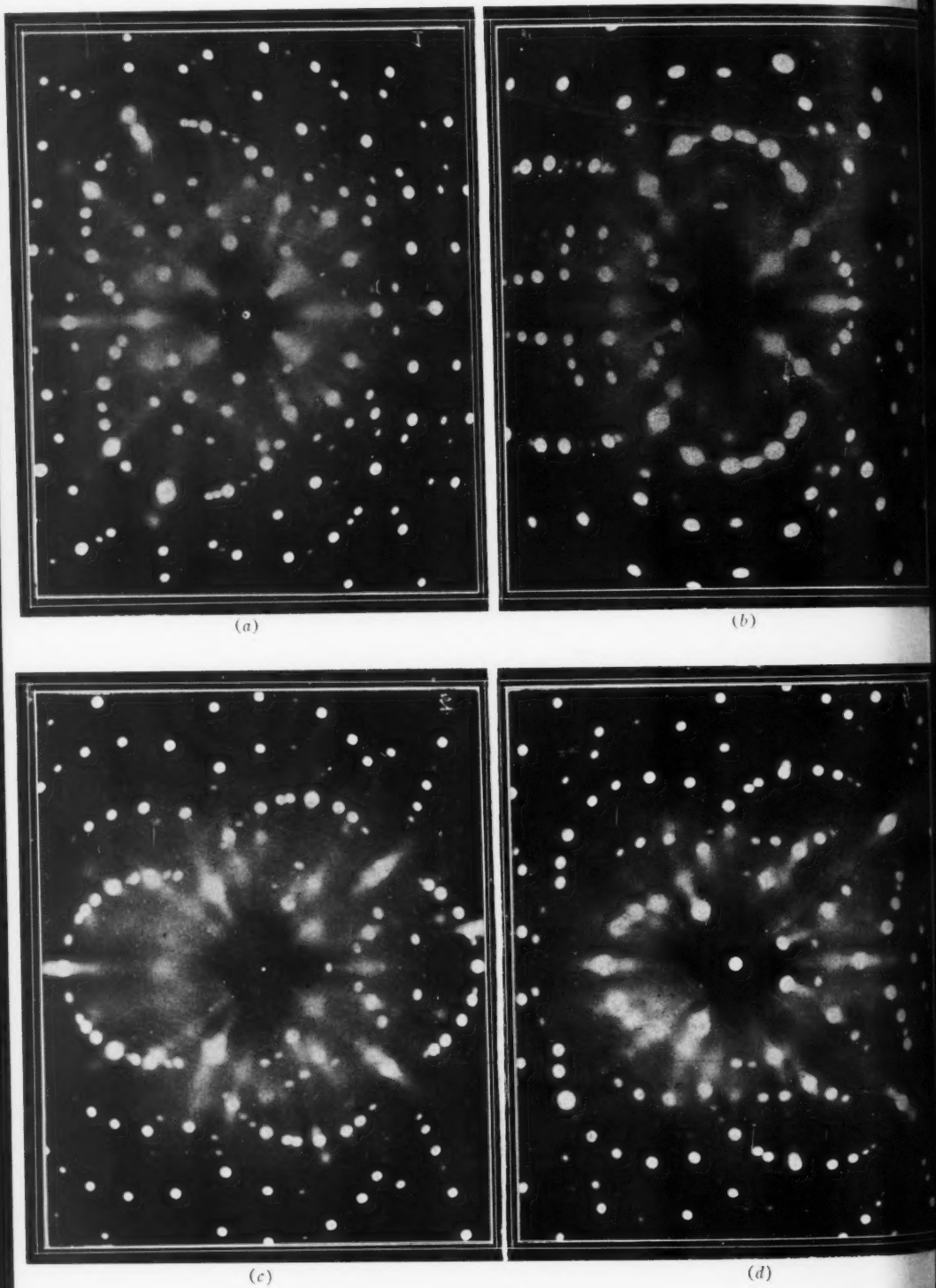


(*a*)
25° C.

FIG. 2

(*b*)
425° C.

Raman X-Ray Reflections in Calcite



(a) (b)

(c) (d)

FIG. 3